In spite of the great advances which have been made in the general methods of detection and determination of ions in inorganic chemistry, the framework within which qualitative analysis is taught to students, and practiced by analysts, has changed little in the last eighty years or so.

In this book Professor Charlot shows how the teaching and practice of qualitative analysis can be put on an entirely new basis, by concentrating all the methods which modern physical chemistry and quantitative analysis, especially colorimetric analysis, make available. The familiar—too familiar—'groups' of the 'classical' system disappear along with most of the (frequently very incomplete) separations on which they were based : most detections are made in solution and extensive use is made of pH and redox potential control, complex formation and extraction with solvents, etc.

As a practical method of qualitative analysis the 'new' method is a great advance, both in speed and efficiency of detection; as a new approach to the teaching of basic physical chemistry it may almost be called revolutionary. Qualitative analysis is a foundation subject through which students still get their first introduction to inorganic chemistry. The classical method requires and provides very little insight into physico-chemical principles, and puts far too much emphasis on the purely descriptive side of the subject. The new method is made a vehicle for teaching basic physical chemistry, and indeed the first part of the book is an excellent introduction to that subject. Thus Professor Charlot has achieved a real integration of what is still looked on too much as the 'purely theoretical' side of chemistry with this not unrelated practical side. based upon twelve years' experience of varying degree of certainty at two chemical schools in Paris.

With 33 diagrams

QUALITATIVE INORGANIC ANALYSIS

G. CHARLOT

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École supérieure de Physique et de Chimie industrielles de Paris

Qualitative Inorganic Analysis

A NEW PHYSICO-CHEMICAL APPROACH

Authorized Translation by
R. C. MURRAY, Ph.D.

FOREWORD

by

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NO teacher of inorganic qualitative analysis who has made any attempt to remain abreast of movements within the subject during the past few years can ignore the uncertainty that exists regarding its precise function in the training of chemists. The 'solution' to the problem adopted by some teachers, particularly in the United States of America—to drop the teaching of qualitative analysis quietly out of the course—is no solution, but is rather a simple evasion of the issues involved. The advances in chemistry during the past twenty years require that serious thought should be given to this matter. On the one hand new analytical techniques have rendered some of the classical methods of analytical chemistry unwieldy and, in many cases, unnecessary, when considered purely functionally. Equally, the improvement in our knowledge of and acquaintance with things previously regarded as unfamiliar—whether these be the elements themselves or our understanding of the physico-chemical principles underlying their behaviour—has made less certain the pedagogical value of the classical course of analysis taught to students.

In this country, on the whole, the response to these doubts has tended to be patchy, and even niggling. Some advances in technique, or some treatment of selected 'less familiar' elements, have been introduced by some teachers dissatisfied with the *status quo*, in an attempt to ensure that at least something of benefit should be derived from the practical course. Where classical theory conflicts with practical results, or where it causes confusion for the student, the teacher often resorts to evasion or to a piecemeal explanation—which in its turn may provide further confusion in other contexts. It is only by individuals that any extensive attempt has been made to introduce modern ideas and to jettison those obsolescent physico-chemical approaches which previously provided much of the pedagogical justification for the classical course. Such individual rebellions have undoubtedly been seriously hampered by the lack of any coherent or ordered body of material on which to base a modern approach.

A glance through the pages of Professor Charlot's book is sufficient to allow the reader to appreciate that it differs markedly from the ordinary run of books on qualitative inorganic analysis. Closer attention to the contents, whether in the theoretical or in the practical part, shows that here is something to provide the groundwork for those teachers who wish to relate their course on qualitative analysis to things as they are. Principles hitherto hardly mentioned in relation to qualitative analysis here receive full treatment, always against a practical

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background; for the reader faced with a world in which titanium and zirconium are as likely to be encountered as chromium or cobalt, no artificial distinction is drawn between familiar and less familiar elements. Whether the student learns the principles in order to improve his analytical abilities, or whether he practises analysis in order to improve his knowledge of the principles, becomes, for the moment, a side issue, since here both are at one with the times.

Whether Professor Charlot has succeeded in producing a generally acceptable approach is something which only time and experience can show; but it seems to me more important that he should have courageously made the attempt in a fashion which must impress his readers with his ability to present a truly up-to-date view of the field. Professor Charlot is already internationally recognized as being amongst the foremost interpreters of physico-chemical principles in their application to qualitative analysis. This book can only serve to make his outstanding abilities in this direction more widely appreciated.

Dr. Murray has done a considerable service to English-speaking readers by making Professor Charlot's work more readily available to them. Through his efforts a book which gives an authoritative and generally acceptable physico-chemical treatment of many of the phenomena of qualitative analysis, according to our present knowledge and understanding of these phenomena, now appears in Britain for the first time.

As one who has the welfare of analytical chemistry much at heart, it is with a very considerable satisfaction that I welcome this translation. Its publication cannot fail to raise the standard of the teaching of qualitative analysis in this country; it likewise cannot fail to emphasize for all chemists the continued value of qualitative analysis in the general training of chemists as a whole.

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PART III

TECHNIQUE AND METHOD OF
QUALITATIVE ANALYSIS

INTRODUCTION

QUALITATIVE analysis has for generations been a foundation subject of chemical training. For most students it serves as an introduction to chemistry as a science: only a small proportion after graduating and leaving a University or Technical High School, etc., take up work in which their main interest is in analysis, whether qualitative or quantitative. Thus the course in analytical chemistry, especially that in qualitative analysis, should be designed to serve both the functions of an introduction to chemistry and as a training for a subsequent career.

It cannot be said that the 'classical' method of qualitative inorganic analysis, based on group separations, performs either of these functions very well. As a method of analysis, and therefore as a specific training for a later career, it is cumbersome, slow, inexact, and messy, whilst as a method of introduction to chemistry it puts too much emphasis on the purely descriptive aspects of the subject.

This need not be so. Qualitative analysis can be made a method of showing students that physical chemistry is of considerable value in the solution of practical problems. Such an integration of the physico-chemical approach to solution chemistry into the teaching of analysis seems to be much overdue and is pregnant with considerable possibilities for the understanding and prediction of chemical processes. It is a main purpose of this book to show how this integration can be achieved.

The 'new' method of qualitative analysis as described in this book makes use of all possible means of detection and characterization, such as pH control, complex formation, adjustment of redox potential, solvent extraction, etc., in addition to that of precipitation which is practically the only one used in the classical method. In this way, fundamental physico-chemical principles are put into practice. Moreover, the new method is considerably more rapid and exact than the classical one.

The book is divided into three parts. In Part I, the general properties of compounds both in solution and in contact with solvents are described and the methods of expressing these properties in quantitative terms are expounded. In Part II the individual properties of the more important ions and compounds and their detection and characterization are dealt with. In Part III will be found details of analytical technique and the methods of conducting an analysis by the new procedure.

Those who want to find out immediately how the system differs in its practical details from the classical one will doubtless turn first to Part III. This part has deliberately been put at the end because, to understand the method properly, Part I must be studied very carefully, and Part II follows logically on Part I.

In the first part an attempt has been made to familiarize the reader with the means which physical and electrochemistry make available for the prediction of the results of reactions in solution. No special knowledge of physical chemistry is necessary since all that is definitely required for following the rest of the book is given in a directly usable form,

Experience with students over a number of years has shown that such an approach is both possible and valuable.

The various types of reaction in solutions are presented in a new form which makes it possible to treat all cases in a similar manner, using the same formulae, which simplifies matters greatly. Reactions involving exchanges of electrons (oxidants and reductants) of ions and molecules (complexes) and, among ions, of protons (acids and bases) are dealt with in sequence. We then proceed to the study of more complicated cases involving several simultaneous exchanges, and finally to cases where more than one phase is involved, including those special cases of great importance in analytical chemistry, the formation of a precipitate and extraction by an immiscible solvent. A special feature is the use of simplified diagrams to represent the effect of *p*H on redox potentials and solubilities, etc., and on the domain of existence of various chemical species.

The unified treatment is extended to indicators which are classified as those of *p*H, redox, and of ionic concentrations. Numerous examples are given to prevent the treatment becoming in any way abstract.

The reader is then made acquainted with the various complicating factors which often make it difficult to make precise statements about precipitations, etc.: condensed ions, ageing of precipitates, slowness of redox reactions, catalysis, etc.

A specially valuable feature of the second part is felt to be the large number of stability constants and redox potentials which are contained in it.

The method of qualitative analysis which we have developed (in collaboration with Mlle Bézier and M. Gauguin) aims at detecting ions independently with a minimum of separation. It resembles in many ways the methods used nowadays in colorimetry, wherein the classical separation of elements into groups has been discarded. Separations are avoided wherever possible by making use of *p*H control, formation of complexes, selective reagents, and organic solvents. When separations are necessary they are made in order to isolate the element sought quantitatively and to discard interfering elements.

No analytical tables of the ordinary type will be found in this book. It is sufficient to refer to each compound in Part II to find the conditions for its characterization. When several substances have to be detected and characterized, several general tests are carried out and then the elements are detected in a given order which is fully set out in Part III.

In qualitative analysis by the usual methods no attempt should be made to look for traces of elements. Indications of the presence of traces are valueless unless accompanied by an estimate of their order of magnitude.

We have thus been able to set as the aim of our method of analysis the detection of each element present whose content exceeds 0·1 or 1 per cent of the original solid, thus to detect one part of the element in the presence of 100 or 1000 parts of each or all of the others.

Among other things the method is not rigid. Each characterization can be replaced by another, according to the circumstances, by using methods similar to those which we have proposed.

Parts II and III indicate the methods to be followed for the detection of most of the cations and anions derived from about 50 elements, which include most of those likely to be met with in a very wide range of natural and artificial materials of present-day economic importance.

The method outlined in this thesis has been put into practice over a period of twelve years of teaching at the École supérieure de Physique et de Chimie industrielles de Paris. In the choice of methods of detection we have been guided to a considerable extent by a form of operational research carried out in the teaching laboratories, examining the results obtained by different methods in practice by a large number of students. The method is now in use in numerous universities and industrial laboratories in France and many parts of the world.

The translation has been prepared from the material for the fourth revised French edition, in which advantage has been taken of recent research to include much new data, and of criticisms by various English readers of the French edition to introduce numerous improvements in the presentation.

It is with great pleasure that I take this opportunity of thanking most sincerely the two persons to whom the appearance of this English edition is mainly due, Dr. R. Belcher, who has followed my work with interest for several years and who first suggested an English translation, and Dr. R. C. Murray, who has not only made the translation but has made a number of criticisms and suggestions for modifications and rearrangement of the text which have been included in it, and will be included in the fourth French edition.

<div style="text-align: right">G. CHARLOT</div>

PART I
THEORY

CONSTITUTION OF ATOMS AND OF COMPOUNDS. OXIDATION NUMBER. CO-ORDINATION NUMBER. CONSTITUTION OF SOLUTIONS

CONSTITUTION OF ATOMS.—Atoms are composed of a nucleus around which electrons circulate in different shells and sub-shells.

The total number of electrons is equal to the atomic number of the element as shown in the periodic classification, a copy of which will be found at the end of this book.

Thus the hydrogen atom possesses only one electron, as shown diagrammatically in fig. 1. The atom of helium, whose atomic number is 2, has two electrons. The corresponding electron shell (K shell) cannot contain more than two electrons; it is then saturated. Lithium has three electrons distributed in two shells (fig. 1); the K shell saturated with two electrons, and one electron in the L shell. Eight electrons are required to saturate the L shell. This number is attained with neon, having the atomic number 10. Sodium, atomic number 11, and chlorine, atomic number 17, are also shown diagrammatically in fig. 1.

FIG. 1

THE ELECTRON. THE PROTON. IONS.—The electron is the elementary charge of negative electricity. It will be represented by the letter e.

The atom itself is neutral, and the negative charge carried by the electrons is compensated by an equal charge carried by the nucleus.

If the atom loses one or more electrons, it becomes positively charged; if it captures electrons, it is then negatively charged. Such charged atoms are called *ions*.

Thus the atom of hydrogen which has lost its electron bears a positive charge: it is the proton. It is a rather special sort of ion, for it consists of nothing else than the nucleus of the atom of hydrogen. It is written (H^+).
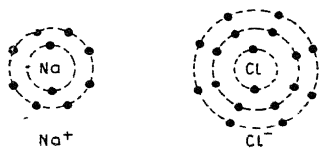
FIG. 2

The atom of sodium can lose an electron, yielding the sodium ion Na^+ (fig. 2). The atom of chlorine can acquire an electron, yielding the ion Cl^- (fig. 2). Similarly the ions Fe^{2+}, Fe^{3+}, S^{2-} can be formed.

BONDS BETWEEN ATOMS IN COMPOUNDS. RULE.—

Atoms are bound to one another by exchanges of electrons; these exchanges occur in such a way as to achieve the most stable electronic configuration, which is, in general, that which corresponds to the saturation of the exterior electron shells; in the majority of cases this is the electronic configuration of the rare gases.

Three principal types of bonds can be distinguished *arbitrarily*.

Covalent (or homopolar) bonds.—Two atoms each supply one electron which they then share in common.

Examples.—In the molecule of hydrogen, the two electrons, one belonging to one atom and one to the other, are shared in common by both. The electron shells of both atoms are thus saturated (helium configuration).

$$H\cdot \ + \ \times H \longrightarrow H \times H \quad \text{written} \quad H\text{—}H$$
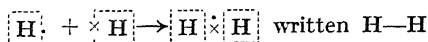
Similarly for the chlorine molecule:

$$\overset{\cdot\cdot \ \ \times\times}{\underset{\cdot\cdot \ \ \times\times}{:Cl \times Cl \times}} \quad \text{or} \quad Cl\text{—}Cl$$

For oxygen:

$$\overset{\cdot \ \cdot \ \times}{\underset{\cdot \ \times \ \times}{:O \ \cdot O \times}} \quad \text{or} \quad O=O$$

For methane:

$$\overset{H}{\underset{H}{H \times C \times H}} \quad \text{or} \quad \overset{H}{\underset{H}{H\text{—}C\text{—}H}}$$
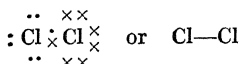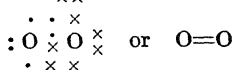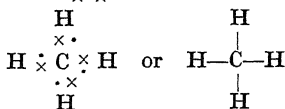
The peripheral shell is saturated by eight electrons for chlorine, oxygen, and carbon.

Co-ordinate (or semi-polar) bonds.—Occasionally one of the atoms alone provides a pair of electrons which are shared with the second atom.

Thus in the formation of the complex ion $NH_4{}^+$, from NH_3 and the ion H^+, the nitrogen furnishes a pair of electrons to the H^+ ion, thereby saturating the exterior shell of electrons in hydrogen:

$$\overset{H}{\underset{H}{H \times N \times}} \ + \ H^+ \longrightarrow \overset{H}{\underset{H}{H \times N \times H^+}}$$
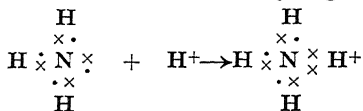
The co-ordinate link is represented by an arrow proceeding from the donor of the electron pair to the acceptor. Thus in the present case, there are, initially, three covalent and one co-ordinate bonds:

$$\overset{H}{\underset{H}{H\text{—}N \longrightarrow H^+}}$$
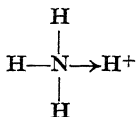
In SO_2 one atom of oxygen is bound to sulphur by two covalent bonds, the other by a co-ordinate one:

$$\overset{\times\times \ \ \cdot\cdot}{\underset{\times\times \ \ \times\cdot \ \times O \times}{\times O : S \times \times}} \quad \text{or} \quad O \leftarrow S = O$$
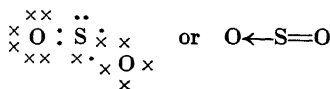
It will be seen that the sulphur still possesses a free pair of electrons, with which it can bind a third atom of oxygen to itself by a co-ordinate bond and SO_3 is obtained:

$$O \atop O{\leftarrow}\overset{|}{S}{=}O$$
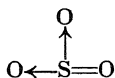
Notes.—(1) G. N. Lewis has adopted the following definitions: 'acid' for the acceptor, and 'base' for the donor of the electron pair. These definitions will not be used in this book.

(2) The separation of the electron pair from the donor atom causes the latter to become positively charged, and the acceptor atom to become negatively charged: hence the name 'semi-polar' for this type of bond:

$$\boxed{A + B \rightarrow A\overset{\alpha+ \quad \alpha-}{\xrightarrow{\hspace{2cm}}}B}$$
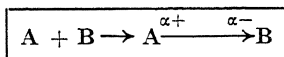
Electrovalent (polar) bonds.—An atom can lose an electron to another atom. For example, in sodium chloride, the atom of sodium has lost an electron to an atom of chlorine, the exterior electronic shells of the two atoms thus becoming saturated. In this way ions are obtained which are linked by electrostatic attraction.

$$Na \cdot \; + \; \overset{\times\times}{\underset{\times\times}{\times}} Cl \overset{\times}{\underset{\times}{\times}} \rightarrow Na \; + \; \overset{\times\times}{\underset{\times\times}{\times}} \overset{}{\underset{}{\cdot}} Cl \overset{\times}{\underset{\times}{\times}}$$
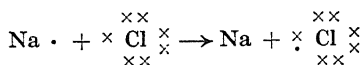
This is written $Na^+....^-\overset{\cdot}{Cl}$.

General case.—Covalencies and electrovalencies represent extreme cases, but in the general case bonds are met with which have the character of both at one and the same time.

Thus in both the covalent and the co-ordinate bond, the shared electrons can be disposed nearer or further from one atom than from the other, as a result of which opposite charges arise on the atoms and finally an electrovalent bond is obtained.

$$H{-}O \atop \phantom{H{-}}\overset{|}{H}$$

Thus, in the molecule of water, the shared electrons in each covalence are nearer to the atom of oxygen than to the atoms of hydrogen; consequently the oxygen is partially negatively, and the hydrogens partially positively, charged; the bond is partially electrovalent.

$$H^{\alpha+}{-}\overset{\alpha-}{\underset{\alpha-}{}}O \atop \phantom{H^{\alpha+}{-}}\overset{|}{\underset{\alpha+H}{}}$$
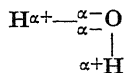
In the case of hydrogen sulphide, H_2S, the same phenomenon is more marked; sulphur is more electronegative than oxygen. On the other hand, the bonds can suffer rearrangement. This happens in the case of NH_4^+, in which the four hydrogen atoms have identical properties; since there were initially three covalent and one co-ordinate bonds, a rearrangement has taken place which has made all the bonds equivalent.

This may be summarized by saying that every intermediate type of bond between the two extremes (of covalent and electrovalent) occurs.

It should also be remarked that the bonds in a given compound may be modified by the ambient medium.

Polarity of molecules.—A molecule is said to be polar if, in the absence of an electric field, the centre of gravity of the negative charges is different from that of the positive charges.

Experience shows that the molecule of water is not symmetric.

$$H \overset{\cdot}{\underset{\cdot}{\times}} \overset{\times}{} \overset{\times}{} \quad H\alpha+ \underset{}{\overset{}{\searrow}} \alpha{-}O$$
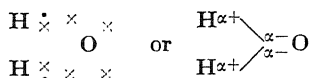
The shared electrons in the covalent bonds are nearer to the atom of oxygen than to the atoms of hydrogen (a state of affairs which is expressed by saying that oxygen is more electronegative than hydrogen), and as a result there are positive charges on the hydrogen atoms and negative ones on the oxygen. As the molecule is not symmetrical, it is a dipole. Numerous molecules are polar: NH_3, H_2O, etc.

$$\boxed{\quad + \qquad - \quad}$$
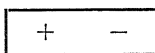
Others, on the other hand, are non-polar: Cl_2, CH_4, etc. But these can also be occasionally polarized by ions or by polar molecules.

Secondary bonds.—The different types of bonds already described do not suffice to explain all the phenomena. Other valencies, termed secondary, have to be postulated. Thus polar or polarized molecules can be attracted or bound in a way that cannot be explained in terms of the basic types of bond.

COMPLEXES.—All substances in solution, whether ions or molecules which contain several atoms, will be termed 'complexes'. Examples are: the ion $NH_4{}^+$, the ion $SO_4{}^{2-}$, the ion $Fe(CN)_6{}^{4-}$, the molecule $HgCl_2$, the molecule HF, etc.

A special type of complex is that known as 'chelate', 'internal', or 'inner' (we shall use the latter term). In this a co-ordinate bond formed between one part of the molecule and another produces a ring. A simple example is given by the compound formed in the well-known dimethylglyoxime test for nickel:

$$
\begin{array}{ccc}
\text{OH} & & \text{O} \\
| & & \uparrow \\
CH_3.C{=}N & \quad N{=}C.CH_3 \\
| & \searrow \quad \swarrow & | \\
& \text{Ni} & \\
| & \swarrow \quad \nwarrow & | \\
CH_3.C{=}N & \quad N{=}C.CH_3 \\
\downarrow & & | \\
\text{O} & & \text{OH}
\end{array}
$$
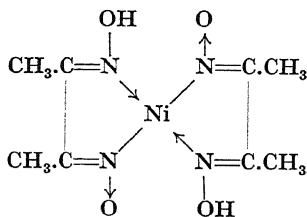
producing a molecule with two five-membered rings.

Note.—The study of the electronic structure of compounds, which has made considerable progress during the course of the last few years, has shed a great deal of light on numerous fields of inorganic and organic chemistry.

Some of the results are relevant to the fields contiguous on analytical chemistry; the inner complexes are nowadays utilized in both qualitative

and quantitative chemistry. There are some rules which make it possible to predict their properties, in particular their solubility in organic solvents and their stability. Consideration of the electronic structures involved permits the prediction of the relative strengths of acids of similar constitution, the stability of certain complexes, etc. It also permits the prediction of certain variations in properties in the periodic classification (see p. 125). The nature of the bonds which are broken in the course of chemical reactions also permits predictions about the rate of reaction. Finally, certain addition reactions can be explained in the light of electronic structure.

But, in the general case of analytical chemistry, restricted to the study and utilization of reactions in solution, electronic structure does not yet help one to predict the quantitative results that are required. It is more profitable to take overall views as a basis without troubling about the true nature of the bonds. In effect, all the bonds are broken in the course of a chemical reaction, the electrons are completely exchanged, and the final result is the same as though electrovalent bonds alone were involved (with a greater or smaller rate of reaction). Consider, for example, the molecule of chlorine: the Cl—Cl bond is broken in the presence of OH^- ions in sufficient quantity; the electrons are separated thus:

$$: \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} \quad + \quad \overset{\times\times}{\underset{\times\times}{\times\, Cl\, \overset{\times}{\underset{\times}{}}}} \quad \text{or} \quad Cl^+ \; Cl^-$$
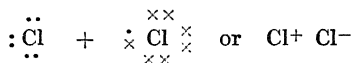
The more the bonds involved approximate to pure covalent ones so much the more difficult is it to find reactions which break them. On the other hand, the more nearly they approach the pure electrovalent type, the more easy is it to cause fission.

OXIDATION NUMBER. OXIDATION STATE.—An atom is said to have the oxidation number N^+ or to be in the N^+ state of oxidation when the ion corresponding has N positive charges, i.e. the atom has lost N electrons. The terms 'electrovalence', or 'valence', are frequently used incorrectly, instead of oxidation number. Thus in ferrous ions, Fe^{2+}, iron has the oxidation number II^+. In hydrogen ions, H^+, hydrogen has the oxidation number I^+.

We generalize without concerning ourselves with ionization. Molecules are neutral, that is to say that the sum total of the charges of ions of which they can be composed is zero.

Examples.—In H_2O we have $2 \times H(I^+)$, and so $O(II^-)$. In manganese dioxide, MnO_2, we have $2 \times O(II^-)$ and so $Mn(IV^+)$. In potassium permanganate, $KMnO_4$, we have $K(I^+)$, $4 \times O(II^-)$, and thus $Mn(VII^+)$. In arsenious oxide, As_2O_3, we have $3 \times O(II^-)$, and thus $As(III^+)$. In arsine, AsH_3, we have $3 \times H(I^+)$, thus $As(III^-)$.

Notes.—(1) The determination of the oxidation number must be based upon chemical properties, i.e. the manner in which the bonds are broken.

Thus in Pb_3O_4 we have $4 \times O(II^-)$, and the 3Pb corresponds to $2 \times Pb(II^+)$ and $1 \times Pb(IV^+)$, i.e. $Pb(PbO_2)_2$.

(2) In certain cases the bonds can be broken differently. Thus in $S_2O_3{}^{2-}$ we can have $S(0)$ and $S(IV)$ or $S(II^-)$ and $S(VI)$.

(3) Most of the bonds met with in organic chemistry are covalences,

and can often be broken in different ways. For simple compounds, it may still be useful to make use of the concept of oxidation number.

Thus in CO_2, we have $C(IV+)$.

In $HCOOH$, we have $C(II+)$.

In HCN, we have $N(III-)$ and $C(II+)$.

In $HCNO$, we have $N(III-)$, $O(II-)$, and $C(IV+)$.

However in organic chemistry it is generally necessary to use more complicated concepts.

INFLUENCE OF SOLVENT. IONS IN SOLUTION

Let us consider solid sodium chloride. In the solid, the ions Na^+ and Cl^- are kept in place by electrostatic attraction.
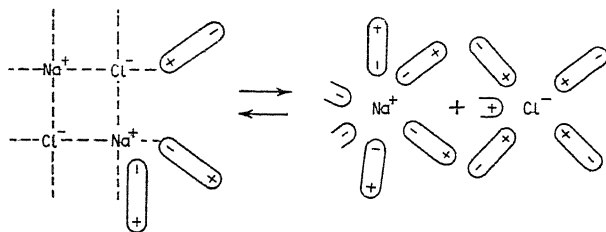
If the molecules of solvent are polar, as in water for example, they also exert attractions on the ions Na^+ and Cl^- and we have the equilibrium:

$$(Na^+,Cl^-) \downarrow + (p + q)H_2O \rightleftharpoons Na^+,pH_2O + Cl^-,qH_2O$$
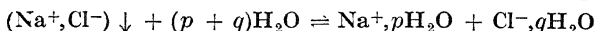
as shown diagrammatically above.

There will therefore be, partially at least, separation and solvation of the particles Na^+ and Cl^-.

The solvation does not depend solely upon the polarity of the molecules, but also on their nature; a true chemical reaction is involved. Thus HCl is not split up into ions by nitrobenzene, although the molecules of the latter are strongly polar.

On the other hand, the higher the dielectric constant of the solvent, and the smaller the attraction between the solvated particles, the more important will solvation be.

Solvation equilibrium is thus the result of a number of properties: polarity of the solvent molecules, charge or polarity of the solute, nature of the bond in the solvated compound, which depends on the nature of the constituents, and the dielectric constant of the solvent.

Electrolytes and non-electrolytes. Ions in solution.—Polar molecules whose charged particles are separated by solvation thus yield, in solution, charged compounds Na^+,pH_2O; Cl^-,qH_2O, which are called solvated ions, or, by a process of simplification, just ions.

Inversely, solvation is necessary for ionization.

Simplified notation.—In general, in order to simplify formulae, we shall represent solvated ions simply by the ion itself. Thus $Al(H_2O)_m{}^{3+}$ will be written Al^{3+}; $Cl(H_2O)_n{}^-$ will be written Cl^-, etc. However, solvation must not be forgotten, for it will have to be used in a certain number of cases.

Constitution of solutions.—During electrolysis, positively charged ions like the sodium ion Na^+ travel towards the cathode: they are called cations. Ions such as the fluoride F^-, nitrate NO_3^- and ferrocyanide $Fe(CN)_6^{4-}$, etc., which travel towards the anode, are called anions.

Solutions can still contain molecules: HF, C_2H_5OH, etc.

Co-ordination number.—The number of molecules or ions grouped around one ion in a complex is not arbitrary. It is often constant for each oxidation number of each element, and it is called the 'co-ordination number'.

The charge carried by the complex is equal to the algebraic sum of the charges carried by its components.

Example.—Cobalt Co(III$^+$) yields numerous complex ions in which the co-ordination number is 6:

$$Co(NH_3)_6{}^{3+}; \quad Co(NH_3)_5Cl^{2+}; \quad Co(NO_2)_6{}^{3-}; \quad Co(H_2O)_6{}^{3+}.$$
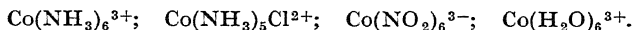
The co-ordination number can be equal to 2, 3, 4, 6, 8, but particularly 4 and 6.

Co-ordination number 6: Fe(III), Co(III), Fe(II), Sn(IV).
,,   ,,   4: Hg(II).
,,   ,,   2: Ag(I).

Notes.—(1) Polyvalent radicals such as $SO_3{}^{2-}$, $SO_4{}^{2-}$, etc., frequently use up several units of the co-ordination number. $SO_3{}^{2-}$, $SO_4{}^{2-}$, NH_2NH_2 generally utilize two units.

(2) This rule was established for solids. In solution the phenomena are slightly different; the solvent, for example H_2O, intervenes, and it is often difficult to define the bonds between the central atom and H_2O. The co-ordination number is then simply a number which it is difficult to exceed.

Example.—Cu(II) has the co-ordination number 4. In ammoniacal solution, we have ammonia complexes. To satisfy the co-ordination rule they can be written $Cu(NH_3)_2(H_2O)_2{}^{2+}$, $Cu(NH_3)_3H_2O^{2+}$, $Cu(NH_3)_4{}^{2+}$. But it is possible to obtain, though with difficulty it is true, $Cu(NH_3)_5{}^{2+}$ in strong NH_3.

For simplicity, the molecules of solvent (in general H_2O) are not given in the formulae of the complexes; a certain number of them can be counted in arriving at the co-ordination number.

CHAPTER II

CHEMICAL EQUILIBRIA. DIFFERENT TYPES OF REACTIONS

RATE OF REACTION. LAW OF MASS ACTION

RECALLING that, in equilibrium,

$$aA + bB + \ldots \rightleftharpoons mM + nN + \ldots$$
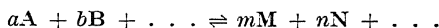
the rate of the forward reaction (left to right) is given by

$$v_1 = k_1 \mid A \mid^a . \mid B \mid^b \ldots$$

and of the reverse reaction (right to left) by

$$v_2 = k_2 \mid M \mid^m . \mid N \mid^n \ldots$$

where k_1 and k_2 are constants and $\mid A \mid, \mid B \mid \ldots \mid M \mid, \mid N \mid, \ldots$ are the concentrations (more exactly the activities) of A, B, M, N, . . .

In equilibrium the two rates are equal and we have

$$v_1 = v_2, \quad \text{and} \quad \frac{k_1}{k_2} = K = \frac{\mid M \mid^m . \mid N \mid^n \ldots}{\mid A \mid^a . \mid B \mid^b \ldots}$$

This is the law of mass action.

Conventions

(1) In all the formulae the concentrations are expressed in gram-ions or gram-molecules per litre.

(2) The constant K is calculated with the products (compounds on the right in the above formula) in the numerator of the expression

$$HF \rightleftharpoons H^+ + F^- \quad K = \frac{\mid H^+ \mid . \mid F^- \mid}{\mid HF \mid}$$
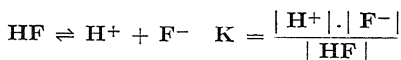
When a substance exists as a solid in the presence of a solution, it is represented by the symbol $\downarrow$, its activity is then constant. This activity is taken by convention as equal to 1, and the values of the constants assume a value corresponding to this.

$$AgCl \downarrow \rightleftharpoons Ag^+ + Cl^-; \quad K = \mid Ag^+ \mid . \mid Cl^- \mid$$
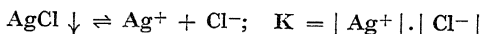
(3) Sometimes the same convention is used when a gas saturates the solution at atmospheric pressure. It is then indicated by the symbol $\uparrow$. This symbol is reserved for the case where the real activity of the compound is not indicated in the formula, but only its partial pressure above the solution, expressed in atmospheres.

$$2Cr^{2+} + 2H^+ \rightleftharpoons 2Cr^{3+} + H_2 \uparrow; \quad K_1 = \frac{\mid Cr^{3+} \mid^2 . pH_2}{\mid Cr^{2+} \mid^2 . \mid H^+ \mid^2}$$
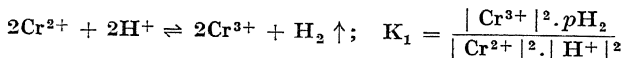
But it is often more convenient to indicate the activity in solution.

$$2Cr^{2+} + 2H^+ \rightleftharpoons 2Cr^{3+} + H_2; \quad K_2 = \frac{\mid Cr^{3+} \mid^2 . \mid H_2 \mid}{\mid Cr^{2+} \mid^2 . \mid H^+ \mid^2}$$
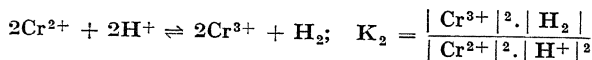
(4) We often have reason to replace activities by concentrations. A particular value of the constant is then obtained, improperly called the 'apparent constant' expressed as K'.

$$HF \rightleftharpoons H^+ + F^-; \quad K' = \frac{C_{H^+} \cdot C_{F^-}}{C_{HF}}$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-; \quad K' = C_{Ag^+} \cdot C_{Cl^-}$$
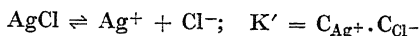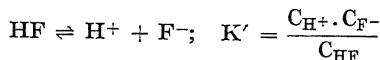
In principle the ionic strength of the solution ought to be indicated in such cases.

SLOW REACTIONS.—The rate of reaction can be low, either when k_1 (or k_2) is small—and the value of k_1 (or k_2) depends on the nature of the substances present,—or when the concentrations are low (equilibrium displaced in one direction).

In analytical chemistry, reagents are in general only allowed to act for a limited period. When reversible reactions are carried out, and equilibrium is rapidly attained, the application of the law of mass action is very useful, and it is this law which makes it possible to predict the phenomena.

Reactions are often slow, and equilibrium is not waited for; sometimes the rate is practically zero. Thus we shall normally find in aqueous solution numerous systems not in mutual equilibrium. Predictions based upon the law of mass action are then no longer valid.

It is thus of great practical importance to have a knowledge of the properties which determine rates of reaction (see p. 108).

ACTIVITY AND CONCENTRATION.—The law of mass action and the laws resulting from it are only correctly expressed if activities and not the concentrations of the ions in question are used.

The activity a is related to the concentration by the expression $a = cf$; f is called the 'activity coefficient'. This coefficient depends more particularly on the concentration of the ion being considered and on its charge. f is smaller the higher the absolute value of the charge on the ion and depends on the nature, charge, and concentration of the other ions present ('ionic strength' of the solution). The following convention is generally adopted: f tends towards unity in very dilute solutions, and consequently it is only in these solutions that activity and concentration can be considered as equivalent.

Calculation of activity coefficients

The 'ionic strength' of the solution is first defined. If $z_1, z_2 \ldots$ represent the charges of the various ions, and $C_1, C_2 \ldots$ their concentrations, the ionic strength I is calculated thus

$$I = \tfrac{1}{2}(z_1^2 C_1 + z_2^2 C_2 + \ldots)$$

Example.—In a solution containing 0·001 g.-mol of KCl per litre, ionizing into K^+ and Cl^-, and 0·001 g.-mol of $MgSO_4$ per litre, ionizing into Mg^{2+} and SO_4^{2-}, we have

$$I = \tfrac{1}{2}(1 \times 0·001 + 1 \times 0·001 + 4 \times 0·001 + 4 \times 0·001) = 0·005$$

Case 1. I is less than 0·02.—f_n is then calculated from the expression

$$- \log f_n = 0·5 z_n^2 \sqrt{I} \qquad (1)$$

It can be seen that, as I approaches 0, f approaches 1. Activities and concentrations become identical.

Example.—In the preceding case we should have:

$$\sqrt{I} = 0·07, \quad \text{whence} \quad - \log f_{k^+} = 0·5 \times 0·07 = 0·035 \text{ or } \log f_{k^+} = \bar{1}·965$$

$$f_k = 0·92 = f_{Cl^-} \quad \text{and} \quad - \log f_{SO_4^{2-}} = 4 \times 0·035 = 0·14;$$

$$\log f_{SO_4^{2-}} = \bar{1}·86; f_{SO_4^{2-}} = f_{Mg^{2+}} = 0·72$$

Case 2. 0·02 $<$ I $<$ 0·2.—The following formula is applicable.

$$- \log f_n = \frac{0·5 z_n^2 \sqrt{I}}{1 + a.0·33.10^8 \sqrt{I}}$$

in which a is the mean radius of the ion under consideration in centimetres. It is generally to be found in tables of constants. Frequently it differs very little from 3.10^{-8} cm., whence

$$- \log f_n = \frac{0·5 z_n^2 \sqrt{I}}{1 + \sqrt{I}}$$

Case 3.—In a concentrated solution, a correction term must be applied

$$- \log f_n = \frac{0·50 Z_i^2 \sqrt{I}}{1 + a.0·33.10^8 \sqrt{I}} + A.I$$

where A varies with the ions.

When the ionic strength increases, f passes through a minimum and then increases with I. It can subsequently become greater than 1.

In practice as soon as the ionic strength becomes sufficient to require serious corrections, formula (1) ceases to be applicable, and the activity coefficients can no longer be calculated a priori.

Note.—Non-ionized molecules, NH_3, HF, etc., have activity coefficients little different from unity when their concentration is less than 0·1 and even when as high as 1 g.-ion per litre.

Activity coefficients

C:	0	5.10^{-3}	10^{-3}	5.10^{-2}	10^{-1}
M^+	1	0·95	0·93	0·85	0·80
M^{2+}	1	0·80	0·74	0·56	0·46
M^{3+}	1	0·62	0·52	0·28	0·20
M^{4+}	1	0·43	0·32	0·11	0·06

DIFFERENT TYPES OF REACTIONS.—Reactions in solution can be divided into two fundamental types:

Electron exchanges or reactions between oxidizing and reducing agents.

Exchanges of ions and of polar molecules, or reactions between

acceptors and donors of the particular particle under consideration. If the particle exchanged is the proton, these are reactions between acids and bases.

Reactions can include the simultaneous exchange of several particles; electrons and protons, electrons and ions, protons and ions, etc.

Equilibria can be displaced by the formation of a second phase: precipitation, liberation of gas, presence of a second non-miscible solvent.

OXIDANTS AND REDUCTANTS
(EXCHANGE OF ELECTRONS)

DEFINITIONS.—Oxidizing agents (always called oxidants) are substances capable of taking up electrons. Reducing agents (always called reductants) are substances which can give up electrons. The relation which defines oxidants and reductants is:

$$\text{Oxidant} + ne \rightleftharpoons \text{Reductant}.$$
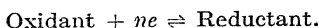
In this way an oxidant-reductant or 'redox' pair is defined.

Examples.—Ferric ions Fe^{3+} are oxidants.

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$
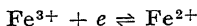
Ferrous ions Fe^{2+} are reductants. Thus this relation defines the ferric—ferrous oxidant-reductant pair. Ferric ions can be reduced to ferrous ions, and ferrous oxidized to ferric.

Oxidation thus corresponds to an increase and reduction to a decrease in the oxidation number. Ferrous iron, in which iron has the oxidation number II^+, is oxidized to the ferric state, in which its oxidation number is III^+.

Stannous salts are oxidized to stannic ones:

$$Sn^{2+} - 2e \longrightarrow Sn^{4+}$$
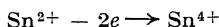
Ferrocyanides are oxidized to ferricyanides:

$$Fe(CN)_6{}^{4-} - e \longrightarrow Fe(CN)_6{}^{3-}$$
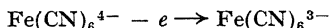
The passage of metals into solution or their precipitation are oxidation-reduction phenomena.

$$Zn \downarrow - 2e \rightleftharpoons Zn^{2+}$$

$$Ag \downarrow - e \rightleftharpoons Ag^+$$
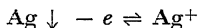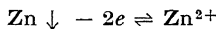
The reduction of hydrogen ions yields hydrogen

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow$$
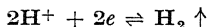
OXIDATION-REDUCTION REACTIONS.—Electrons do not exist in the free state in solution. In order for an oxidant to be able to gain electrons, a reductant which can lose electrons to it must be present. Representing the oxidant by Ox_1 and the reductant with which it reacts by Red_2, we have the two oxidation-reduction systems.

$$aOx_1 + ne \longrightarrow aRed_1$$
$$\underline{bRed_2 - ne \longrightarrow bOx_2}$$
$$aOx_1 + bRed_2 \longrightarrow aRed_1 + bOx_2$$
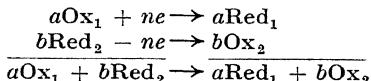
Example.—Thus, stannous ions in proximity to ferric ions give up

their electrons which are taken up by the ferric ions. Ferric salts are reduced by stannous salts.

$$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+}$$
$$\underline{Sn^{2+} - 2e \longrightarrow Sn^{4+}}$$
$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$
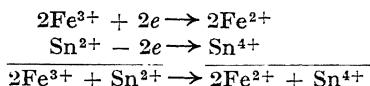
The chemical equations can be balanced by considering the numbers of electrons exchanged or transferred.

CELL. ELECTROLYSIS.—Electrons can be brought into action by physical means: (1) by constructing a cell, and (2) by electrolysis.

Imagine a cell divided into two compartments by a wall which permits the passage of current but prevents the mixing of the two solutions. Suppose inert electrodes A and B to be placed in the solutions, and joined by an external wire (fig. 3).

FIG. 3

If a ceric salt Ce^{4+} be introduced into compartment A and a ferrous salt Fe^{2+} into B, current flows through the wire from A to B, which means that electrons flow through it from B to A. They are given up by the ferrous salt which is oxidized:

$$Fe^{2+} - e \longrightarrow Fe^{3+}$$
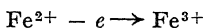
and are taken up by the ceric salts which are reduced:

$$Ce^{4+} + e \longrightarrow Ce^{3+}$$
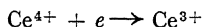
The reaction which is brought about in this manner is:

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$
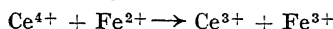
STRENGTH OF OXIDANTS AND REDUCTANTS IN OXIDANT-REDUCTANT PAIRS.—An oxidant is the stronger the more easily it can take up electrons. The more energetically the oxidant takes up electrons, the less easily the conjugate reductant gives them up, or, put differently, the more easy the oxidant is to reduce, the more difficult its conjugate reductant is to oxidize, or again, the stronger the oxidant, the weaker the conjugate reductant. In the system: $Ce^{4+} + e \rightleftharpoons Ce^{3+}$, Ce^{4+} is a strong oxidant, and Ce^{3+} is a weak reductant. In the system: $Ti^{4+} + e \rightleftharpoons Ti^{3+}$, Ti^{3+} is a strong reductant, it reduces numerous oxidants; Ti^{4+} is a weak oxidant, and cannot be reduced by many substances.

These remarks apply only where the system is a reversible one.

Oxidation-reduction potential.—This is the parameter which makes it possible to classify precisely the oxidizing and reducing strengths of different systems.

To the system $Ox + ne \rightleftharpoons Red$ corresponds the potential

$$E = E_0 + \frac{RT}{nF} \log_e \frac{|\, Ox\,|}{|\, Red\,|}$$

It is this potential E which controls the exchange of electrons. This potential can be made evident by constructing a cell of the sort indicated above. The electrodes must be inert, i.e. they must be non-oxidizable ones, which means that they cannot send ions into solution, which would
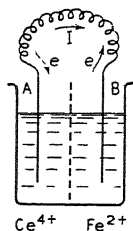
bring into action electrons foreign to the system under consideration. Their sole function must be to permit the electrons belonging to the systems already in solution to circulate. Polished platinum and gold are suitable since they are not oxidizable. Between the two electrodes of the cell there is a difference of potential $E_A - E_B$, E_A being the potential of the electrode A with respect to the solution of ceric salt, and E_B that of the electrode B with respect to the solution of ferrous salt. If $E_A > E_B$, current passes from A to B, as a result of which the ceric salt will be reduced and the ferric salt oxidized, according to the reaction

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$
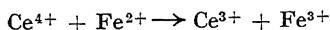
The potential of each electrode with respect to the solution in which it dips (or rather with respect to a reference electrode which is taken as the origin of the potentials) can be determined and is called the oxidation-reduction potential of the solution. When one solution has a higher oxidation-reduction potential than another solution, a cell can be formed and the second solution can be oxidized by the first. *The result is the same if the solutions are mixed.* Thus the potential represents the oxidizing power of the solution.

The oxidation-reduction system ferrous ion–ferric ion is reversible. Fe^{3+} is the oxidant and Fe^{2+} the reductant. In chemical reactions Fe^{3+} is sometimes reduced and Fe^{2+} sometimes oxidized.

As might be expected, the oxidation-reduction potential depends on both the concentration of Fe^{3+} and on that of Fe^{2+}. The higher the proportion of ferric in relation to ferrous iron, the more oxidizing is the solution and the higher the potential. The formula for the oxidation-reduction potential, confirmed by experiment, is:

$$E = E_0 + \frac{RT}{nF} \log_e \frac{| \text{Oxidant} |}{| \text{Reductant} |}$$

E_0 is a constant, R the gas law constant, T the absolute temperature, n the number of electrons brought into action, F the Faraday, | Oxidant | and | Reductant | the activities of oxidant and reductant.

Replacing the letters by their values at 15° C., and transforming the Napierian logarithms to decimal ones, we get:

$$E = E_0 + \frac{0 \cdot 058}{n} \log \frac{| \text{Ox} |}{| \text{Red} |}$$

In the case where the oxidation-reduction system is represented by: $a\text{Ox} + ne \longrightarrow b\text{Red}$, we have:

$$E = E_0 + \frac{0 \cdot 058}{n} \log \frac{| \text{Ox} |^a}{| \text{Red} |^b}$$

$$E = E_1 + 0 \cdot 06 \log \frac{| Fe^{3+} |}{| Fe^{2+} |}$$

$$E = E_2 + 0 \cdot 03 \log \frac{| Tl^{3+} |}{| Tl^+ |}$$

$$E = E_3 + 0 \cdot 03 \log \frac{| H^+ |^2}{| H_2 |}$$

When the potential of the system is measured with a hydrogen elec-

trode (platinized platinum saturated with hydrogen at normal pressure), we have: $|\,H_2\,|$ = constant, and:

$$E = E'_3 + 0.06 \log |\,H^+\,|$$

By convention we take $E = 0$ in this latter case for $|\,H^+\,| = 1$ (normal hydrogen electrode). All oxidation-reduction potentials are therefore determined with respect to that of the normal hydrogen electrode = 0.

Normal potential.—When $\dfrac{|\,Ox\,|}{|\,Red\,|} = 1$, the potential of the system becomes equal to E_0. This is the normal potential which has a definite value for each system. Thus we have:

$$E = 0.78 + 0.06 \log \frac{|\,Fe^{3+}\,|}{|\,Fe^{2+}\,|} \text{ volt}$$

0·78 volt is the value of the potential for $|\,Fe^{3+}\,| = |\,Fe^{2+}\,|$.

Prediction of reactions.—We have seen that the value of the oxidation-reduction potential of a solution makes it possible to predict reactions when a cell is formed or when the solutions are mixed. Thus ceric salts oxidize ferrous salts, for we have:

$$E_1 = 1.68 + 0.06 \log \frac{|\,Ce^{4+}\,|}{|\,Ce^{3+}\,|} \text{ volt}$$

$$E_2 = 0.78 + 0.06 \log \frac{|\,Fe^{3+}\,|}{|\,Fe^{2+}\,|} \text{ volt}$$

During the reaction the ratio $\dfrac{|\,Ce^{4+}\,|}{|\,Ce^{3+}\,|}$ decreases, hence E_1 decreases, and the ratio $\dfrac{|\,Fe^{3+}\,|}{|\,Fe^{2+}\,|}$ increases, therefore E_2 increases. The reaction ceases when $E_1 = E_2$.

Some normal potentials in aqueous solution :

$$
\begin{array}{rcll}
Co(CN)_6{}^{3-} + & e \rightleftharpoons & Co(CN)_6{}^{4-} & -\,0.83 \text{ volt} \\
Cr^{3+} + & e \rightleftharpoons & Cr^{2+} & -\,0.41 \text{ ,,} \\
V^{3+} + & e \rightleftharpoons & V^{2+} & -\,0.21\text{-}0.25 \text{ volt} \\
2H^+ + & e \rightleftharpoons & H_2 \uparrow & 0.00 \text{ volt } (H_2 = 1 \text{ atm.} \\
& & & \text{pressure)} \\
Cu^{2+} + & e \rightleftharpoons & Cu^+ & +\,0.16 \text{ volt} \\
Fe(CN)_6{}^{3-} + & e \rightleftharpoons & Fe(CN)_6{}^{4-} & 0.36 \text{ ,,} \\
MnO_4{}^- + & e \rightleftharpoons & MnO_4{}^{2-} & 0.54 \text{ ,,} \\
I_2 + 2e \rightleftharpoons & & 2I^- & 0.62 \text{ ,,} \\
Fe^{3+} + & e \rightleftharpoons & Fe^{2+} & 0.78 \text{ ,,} \\
2Hg^{2+} + 2e \rightleftharpoons & & Hg_2{}^{2+} & 0.91 \text{ ,,} \\
Br_2 + 2e \rightleftharpoons & & 2Br^- & 1.09 \text{ ,,} \\
Tl^{3+} + 2e \rightleftharpoons & & Tl^+ & 1.28 \text{ ,,} \\
Cl_2 + 2e \rightleftharpoons & & 2Cl^- & 1.41 \text{ ,,} \\
Ce^{4+} + & e \rightleftharpoons & Ce^{3+} & 1.68 \text{ ,,} \\
Pb^{4+} + 2e \rightleftharpoons & & Pb^{2+} & 1.75 \text{ ,,} \\
Co^{3+} + & e \rightleftharpoons & Co^{2+} & 1.82 \text{ ,,} \\
Ag^{2+} + & e \rightleftharpoons & Ag^+ & 1.98 \text{ ,,} \\
F_2 + 2e \rightleftharpoons & & 2F^- & 2.8 \text{ (calculated)}
\end{array}
$$

Notes.—(1) Oxidants are classified in order of increasing, and the reductants in order of decreasing, strength.

An oxidant can react with any reductant which is above it in the table. However, we shall see that in quantitative analysis for the reaction to be practically complete, it is necessary for the potential difference between the two systems to be 0·20–0·40 volt, according to the number of electrons exchanged.

Note that in the system $F_2/2F^-$, F^- is a reductant. But it can only reduce systems having a higher potential than itself, and there are hardly any. Similarly Ce^{3+} can act as a reductant in acid solution only towards oxidants more energetic than Ce^{4+}, i.e. in a limited number of cases. It is a poor reductant. At the other end of the scale Cr^{3+}, for example, is a poor oxidant. On the other hand, systems placed in the centre of the table can oxidize a large number of systems and reduce a large number also. Thus for the system Fe^{3+}/Fe^{2+}, Fe^{3+} is the oxidant and Fe^{2+} the reductant in a large number of cases.

(2) The most energetic oxidant, F_2, can only be obtained by electrolysis. It oxidizes all the other systems. It acts on the ions of water:

$$2F_2 \uparrow\ +\ 2O^{2-} \longrightarrow 4F^- + O_2 \uparrow$$
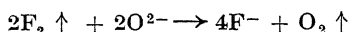
(3) Some systems have an extremely small rate of reaction, and they hardly act at all as their normal potential would indicate (see p. 108).

(4) We are dealing here with the normal potential which must not be confused with the formal potential used in practice (see p. 19).

(5) In the formulae, activities and not concentrations should be used. The effect of salts is far from being always negligible, particularly with polyvalent ions. Thus the ferri–ferrocyanide system at a concentration of $M/300$ has a potential of 0·4 volt in a neutral medium. In the presence of 2M potassium chloride, the potential is 0·5 volt.

(6) We are dealing here with hydrated ions and consequently the values given are only valid in aqueous solution.

OXIDATION-REDUCTION SYSTEMS OF WATER.—In principle, water and its ions can also exchange electrons. There are two oxidation-reduction systems of water:

(1) Water acts as the oxidant:

$$2H^+ + 2e \longrightarrow H_2 \uparrow \quad \text{or} \quad 2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$$
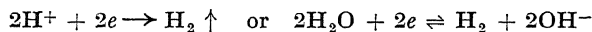
with $E = +0.06 \log |H^+|$ at atmospheric pressure.

(2) Water acts as the reductant:

$$2O^{2-} - 4e \longrightarrow O_2 \uparrow \quad \text{or} \quad 2H_2O - 4e \rightleftharpoons O_2 + 4H^+$$
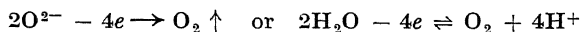
with $E = 1.23 + 0.06 \log |H^+|$ volt (see p. 60) in air.

But generally the reactions are very slow in the absence of catalysts, and the ions of water do not come to equilibrium with the dissolved oxidants or reductants. In general water is inert from the point of view of oxidation-reduction. In many cases its action can be neglected.

Very strong oxidants and very strong reductants.—However, there are exceptions in the form of very strong oxidants and very strong

reductants. They react with water perceptibly and consequently cannot exist for long in aqueous solution. Thus F_2 does not exist in solution in water. It immediately takes up electrons quantitatively to give F^-, which does not act as a reductant; in aqueous solution it does not show any tendency to give up electrons.

$$F_2 \uparrow + 2e \rightleftharpoons 2F^-$$
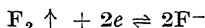
and we have :
$$2F_2 \uparrow + 2O^{2-} \longrightarrow 4F^- + O_2 \uparrow$$

Na is a very strong reductant. It does not exist in water. Reciprocally, Na^+ has lost its oxidizing properties:

$$Na \downarrow - e \longrightarrow Na^+$$
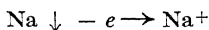
and we have :
$$2Na \downarrow + 2H^+ \longrightarrow 2Na^+ + H_2 \uparrow$$

FORMAL POTENTIAL.—Consider the ferrous-ferric system. We have:

$$E = E_0 + 0{\cdot}058 \log \frac{\mid Fe^{3+} \mid}{\mid Fe^{2+} \mid}$$

where $\mid Fe^{3+} \mid$ and $\mid Fe^{2+} \mid$ represent the activities of the ions Fe^{3+},aq. and Fe^{2+},aq., respectively.

Assume they are present in M-HCl solution. Part of the ferric iron is present as Fe^{3+} ions, but it is also present as $FeOH^{2+}$, $FeCl^{2+}$, $FeCl_6^{3-}$, etc. Similar remarks apply to Fe^{2+}.

Let α and β be the fractions of total ferric and total ferrous iron which are present as Fe^{3+},aq. and Fe^{2+},aq. ions.

The potential is given by:

$$E = E_0 + 0{\cdot}058 \log \frac{\alpha \times C_{eF(III)} \times f_{Fe}^{3+}}{\beta \times C_{Fe(II)} \times f_{Fe}^{2+}}.$$

If E_0 is the normal potential (zero ionic strength), $C_{Fe(III)}$ and $C_{Fe(II)}$ are the total concentrations of ferric and ferrous iron which are all that are available to us and f_{Fe}^{3+}, f_{Fe}^{2+} are activity coefficients. We then have:

$$E = E_0 + 0{\cdot}058 \log \frac{\alpha}{\beta} + 0{\cdot}058 \log \frac{f_{Fe}^{3+}}{f_{Fe}^{2+}} + 0{\cdot}058 \log \frac{C_{Fe(III)}}{C_{Fe(II)}}$$

or, under given conditions:

$$E = E_1 + 0{\cdot}058 \log \frac{C_{Fe(III)}}{C_{Fe(II)}}.$$

Thus we define E_1, the formal normal potential which is valid for particular given conditions and which makes it possible to calculate the potential from the concentrations, which are all that are known. This value is also used in conditions which approach those where it is strictly valid. The value of E_1 should always be accompanied by an indication of the solution to which it corresponds.

Examples.—In the ferrous-ferric system, the value of E_0 is 0·78 volt.

In M-HClO$_4$ or M-HNO$_3$	.	.	0·70 volt
M-HCl .	. . . .	.	0·65 ,,
M-H$_2$SO$_4$.	. . . .	.	0·61 ,,

Some values of formal potentials

$Ce(IV) + e \rightleftharpoons Ce(III)$ $E_0 = 1\cdot 68$ volts
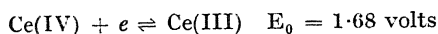
$9N\text{-}HClO_4$	$1\cdot 90$ volts
$N\text{-}HClO_4$	$1\cdot 70$,,
$N\text{-}HNO_3$	$1\cdot 61$,,
$M\text{-}H_2SO_4$	$1\cdot 44$,,
$N\text{-}HCl$	$1\cdot 28$,,

$Sn(IV) + 2e \rightleftharpoons Sn(II)$
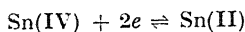
$N\text{-}HCl$ . . . . $\sim$	$0\cdot 15$ volt
$0\cdot 1N\text{-}HCl$	$0\cdot 07$,,
$9N\text{-}H_2SO_4$	$0\cdot 40$,,

$Fe(CN)_6{}^{3-} + e \rightleftharpoons Fe(CN)_6{}^{4-}$ $E_0 = 0\cdot 36$ volt
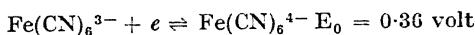
$N\text{-}HCl$	$0\cdot 71$–$0\cdot 77$ volt
$0\cdot 1N\text{-}HCl$	$0\cdot 56$–$0\cdot 69$,,
$N\text{-}H_2SO_4, N\text{-}HClO_4$	$0\cdot 72$ volt
$0\cdot 01N\text{-}NaOH$	$0\cdot 46$,,
$5N\text{-}NaOH$	$0\cdot 52$,,

A large number of formal normal potential values will be found in the second part of this book.

OXIDATION-REDUCTION POTENTIAL OF OXIDIZING AND REDUCING SOLUTIONS

In the system:

$$\text{Oxidant} + ne \rightleftharpoons \text{reductant}$$
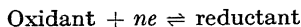
we have $$E = E_0 + \frac{0\cdot 058}{n} \log \frac{|\text{ Ox }|}{|\text{ Red }|}$$

Let us vary the ratio of $|\text{ Ox }|/|\text{ Red }|$ from 0 per cent oxidant and 100 per cent reductant to 100 per cent oxidant and 0 per cent reductant, the sum of the two remaining constant. We obtain the curve shown in fig. 4, which is of the form

$$y = a + b \log \frac{x}{c - x}$$

Potential of a solution containing conjugate oxidants and reductants. Buffer solutions.—The potential is given by the preceding formula. Such a solution, which contains at the same time conjugate oxidant and reductant, is called a buffer solution. The addition to this solution of an oxidant or a reductant in quantity sufficient to cause a considerable variation of the $|\text{ Ox }|/|\text{ Red }|$ ratio only changes the potential by a small amount (fig. 4).

Example.—Consider a solution containing a ferric and a ferrous salt each at unit concentration. We have:

$$E = 0\cdot 78 + 0\cdot 06 \log \frac{|\text{ Fe}^{3+}|}{|\text{ Fe}^{2+}|} = 0\cdot 78 \text{ volt}$$

Suppose that a powerful reductant be added, for example Cr^{2+} at a concentration of 10^{-1}, then:
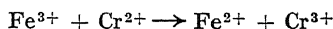
$$Fe^{3+} + Cr^{2+} \longrightarrow Fe^{2+} + Cr^{3+}$$
$$| Fe^{3+} | = 1 - 0.1$$
$$| Fe^{2+} | = 1 + 0.1$$
$$E = 0.78 + 0.06 \log \frac{1 - 0.1}{1 + 0.1} = 0.77 \text{ volt}$$

The potential is little changed.

The same result would be obtained if a powerful oxidant were added, for example Ce^{4+}.

Such solutions containing conjugate oxidant and reductant make it possible in practice to maintain the oxidation-reduction potential at a given value.
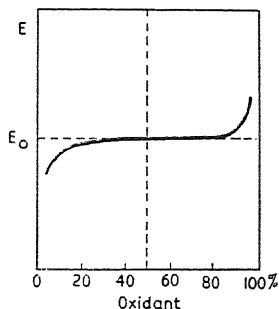
FIG. 4.—$E = E_0 + 0.06 \log \dfrac{| Ox |}{| Red |}$

Experiment.—Consider a buffer mixture $Sn(II)/Sn(IV)$, 0.15 volt in HCl. Add to it ferrous *o*-phenanthroline complex (red—1·10 volts —pale blue). The solution turns red. Add some ceric salt ($E = 1.28$ volts). A large quantity of ceric salt is necessary before 1·10 volts is reached and the indicator changes colour.

On the other hand, in a solution of N-HCl, coloured red by one drop of ferrous *o*-phenanthroline, 1 drop of ceric salt causes the potential to rise rapidly and the indicator changes.

Potential of an oxidant or a reductant.—In the formula

$$E = 0.78 + 0.06 \log \frac{| Fe^{3+} |}{| Fe^{2+} |} \text{ volt}$$

if we make $| Fe^{2+} | = 0$, i.e. a pure solution of ferric ions, we get $E = + \infty$.

In practice, it is impossible to obtain pure Fe^{3+} for two reasons: (1) no oxidant sufficiently powerful to oxidize the last traces of Fe^{2+} can be found; and (2) when the potential becomes very high, water acts as a reductant. In practice, we cannot exceed 1·5 volts.

Mixture of two oxidants and two reductants.—Consider the mixture of ceric and ferric salt, $Ce^{4+} + Fe^{3+}$. When a reductant is introduced, the most oxidizing compound is first reduced.

The potential is given here by Ce^{4+}.

Note.—For a certain number of compounds, rates of reaction have to be taken into account (see p. 108).

Mixture of the oxidant from one system and the reductant from another.—When the reductant Red_2 is added to the oxidant Ox_1 the reaction which occurs is:
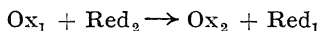
$$Ox_1 + Red_2 \longrightarrow Ox_2 + Red_1$$

As much Ox_2 as Red_1 is produced, hence $| Ox_2 | = | Red_1 |$. If Ox_1 and Red_2 are mixed in equal proportions, after reaction there remains $| Ox_1 | = | Red_2 |$.

On the other hand, at equilibrium the potentials of the two systems are equal, and we have:

$$E = E_1 + 0.06 \log \frac{| Ox_1 |}{| Red_1 |} = E_2 + 0.06 \log \frac{| Ox_2 |}{| Red_2 |}$$

or $\quad 2E = E_1 + E_2 + 0.06 \log \dfrac{| Ox_1 |}{| Red_1 |} \times \dfrac{| Ox_2 |}{| Red_2 |} = E_1 + E_2$

$$E = \frac{E_1 + E_2}{2}$$

under the particular conditions indicated above.

More generally, to the equilibrium:

$$aOx_1 + bRed_2 \rightleftharpoons aRed_1 + bOx_2$$
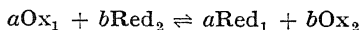
corresponds the potential

$$E = \frac{bE_1 + aE_2}{a + b}$$

POLYOXIDANTS, AMPHOLYTES, DISPROPORTIONA-TION.—A given element can exist in several states of oxidation, and consequently can exchange several electrons in succession.

Vanadium can have the oxidation numbers II^+, III^+, IV^+, and V^+ and we can have

$$V(II^+) - e \rightleftharpoons V(III^+)$$
$$V(III^+) - e \rightleftharpoons V(IV^+)$$
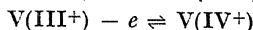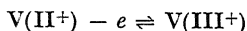
$V(II^+)$ is a polyreductant, and can be reduced with exchange of several electrons:

$$V(II) - 2e \longrightarrow V(IV)$$
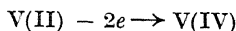
Similarly $V(IV)$ is a polyoxidant.

Let us call E_4 the normal potential corresponding to $V(IV)/V(III)$ and E_3 the normal potential corresponding to $V(III)/V(II)$, we then have:

$$E = E_4 + 0.06 \log \frac{| V(IV) |}{| V(III) |}$$

and $\quad\quad\quad\quad E = E_3 + 0.06 \log \dfrac{| V(III) |}{| V(II) |}$

It appears that it can always be said, so long as *simple ions* such as V^{3+},aq. or V^{2+},aq. are being dealt with, that the highest state of oxidation is also the most powerfully oxidizing one and that it is more easy to accept the first electron. Thus, in principle, $E_4 \geqslant E_3$.

$V(III)$ is the oxidant in the first system above and it can accept an

electron to give V(II). It is the reductant in the second system and can donate electrons in order to give V(IV).

A species such as V(III), which can sometimes accept, and sometimes donate a particle, is called an 'ampholyte' and we have the equilibria:

$$V(III) + e \rightleftharpoons V(II)$$
$$\underline{V(III) - e \rightleftharpoons V(IV)}$$
$$V(III) + VIII \rightleftharpoons V(IV) + V(II)$$
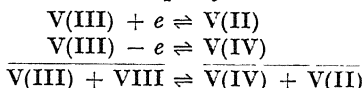
This is the **disproportionation** equilibrium.

We shall see that the equilibrium can be displaced towards the right by the disappearance of V(IV) or V(II). V(III) then disappears. It is said to be disproportionated. Sometimes it can be almost completely disproportionated; under such conditions the (III)$^+$ state of oxidation ceases to exist.

Potential of a solution of an ampholyte.—Consider, for example, a solution of V(III). We have:

$$V(III) + e \rightleftharpoons V(II) \quad E_3 = -0.20 \text{ volt}$$
$$V(III) - e \rightleftharpoons V(IV) \quad E_4 = 0.40 \quad ,,$$
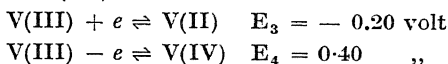
V(III) is the oxidant of one system and the reductant of another. Its concentration is obviously the same in both cases.

$$E = \frac{E_3 + E_4}{2} = \frac{-0.20 \text{ volt} + 0.40 \text{ volt}}{2} = 0.10 \text{ volt}$$

The potential is independent of the concentration.

NORMAL OXIDIZING AND REDUCING SOLUTIONS.—The term 'normal oxidizing solution' is applied to a solution of an oxidant which can take up 1 g.-electron per litre. The concentration in normality is indicated by the letter N.

Thus ferric iron is an oxidant, it fixes an electron.

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$
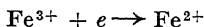
A normal oxidizing solution of ferric iron, Fe(III), is also a molar solution of Fe(III) (indicated M-Fe(III)).

Bromine is an oxidant according to the scheme

$$Br_2 + 2e \longrightarrow 2Br^-$$
$$0.1M\text{-}Br_2 = 0.2N\text{-}Br_2$$
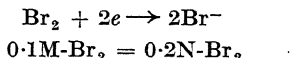
Analogous definitions can be applied to reducing solutions.

General note.—In this chapter the expressions 'take up' and 'give up' electrons have been used. It is customary, however, to say that electrons (or protons or atoms, molecules, ions, etc.) are 'accepted' and 'donated' and these expressions will be used in the rest of the book.

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CHAPTER IV

ACIDS AND BASES (EXCHANGE OF PROTONS)

DEFINITIONS.—Acids are substances which can donate protons. Bases are substances which can accept protons. The relation which defines acids and bases is:

$$\text{Acid} \rightleftharpoons \text{Base} + \boxed{H^+}$$

Thus we define an acid-base pair.

Example.—To the acid HF (hydrofluoric acid) corresponds the base F^- (the fluoride ion).

$$\underset{\text{Acid}}{HF} \rightarrow \underset{\text{Base}}{F^-} + \boxed{H^+}$$
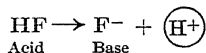
To the ammonium ion NH_4^+, an acid, corresponds the base, ammonia, NH_3:

$$NH_4^+ \rightleftharpoons NH_3 + \boxed{H^+}$$

Aniline is a base in the equilibrium:

$$C_6H_5NH_2 + \boxed{H^+} \rightleftharpoons C_6H_5NH_3^+$$
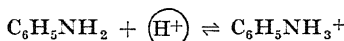
The aluminium ion is an acid in aqueous solution:

$$Al^3,H_2O \rightleftharpoons Al(OH)^{2+} + \boxed{H^+}$$
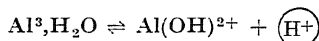
The hydrosulphide ion is a base:

$$S^{2-} + \boxed{H^+} \rightleftharpoons HS^-$$
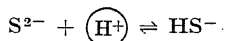
Caustic soda is a base:

$$NaOH + \boxed{H^+} \rightleftharpoons Na^+, H_2O$$
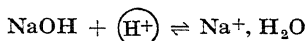
The molecules of ionizing solvents also act as acids and bases; thus water behaves as a base in the equilibrium:

$$H_2O + \boxed{H^+} \rightleftharpoons H_3O^+ \quad (\text{solvated } \boxed{H^+})$$
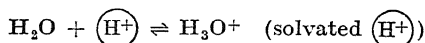
$\boxed{H^+}$ is the proton; H_3O^+ is the hydronium ion or the hydrated hydrogen ion, usually referred to as the hydrogen ion. It symbolizes the action of the polar molecules of water on the proton.

Reactions between acids and bases or of neutralization.— Protons can scarcely exist in the free state. For an acid to donate protons a base capable of accepting them must be present. Consider the acid_1 reacting with a base_2. We shall have the two acid-base systems:

$$\text{Acid}_1 \rightleftharpoons \text{Base}_1 + \boxed{H^+}$$

and

$$\text{Base}_2 + \boxed{H^+} \rightleftharpoons \text{Acid}_2$$

whence

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

There is an equilibrium between the two acid-base systems.

Example.—

$$HF \rightleftharpoons F^- + \boxed{H^+}$$

$$NH_3 + \boxed{H^+} \rightleftharpoons NH_4^+$$

$$\overline{HF + NH_3 \rightleftharpoons F^- + NH_4^+}$$

STRENGTH OF ACIDS AND BASES.—An acid is stronger in proportion as its property of losing protons is more marked. The stronger the acid, the weaker the base. We shall see a precise definition of the strength of acid-base pairs in aqueous solution.

Note.—All the preceding may be applied whatever the solvent.

Aqueous solutions.

Water can behave as an acid:

$$H_2O \rightleftharpoons OH^- + \boxed{H^+}$$

and as a base: $H_2O + \boxed{H^+} \rightleftharpoons H_3O^+$ (hydration of the proton)

Thus we also have the equilibrium:

$$2H_2O \rightleftharpoons OH^- + H_3O^+$$

In aqueous solution, this differentiates the phenomena of proton exchange from those of electron exchange (see p. 18).

Hydrolysis.—When an acid is introduced into water, it can lose protons, because the water molecule can fix them, and we have the equilibrium:

$$Acid + H_2O \rightleftharpoons Base + H_3O^+ \quad . \quad . \quad . \quad . \quad (I)$$

When a base is introduced into water, it can accept protons because the water molecules can donate them to it:

$$Base + H_2O \rightleftharpoons Acid + OH^-$$

This equilibrium is equivalent to the one above since we always have:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The action of water is called hydrolysis, and is exerted both on acids and bases. More exactly this equilibrium depends on the acid-base pair.

Strength of acid-base pairs

Applying the law of mass action to the equilibrium (I) above, we have:

$$\frac{|\,Base\,|\,.\,|\,H_3O^+\,|}{|\,Acid\,|\,.\,|\,H_2O\,|} = K_A$$

The activity of water, $|\,H_2O\,|$, which is very high, 1000/18, remains sensibly constant in dilute solutions. We can thus write:

$$\frac{|\,Base\,|\,.\,|\,H_3O^+\,|}{|\,Acid\,|} = K_A$$

K_A thus defined is called the acidity constant of the acid-base pair. It is more convenient to use $pK_A = -\log K_A$.

An acid is stronger, the more easily it donates its protons, the more the equilibrium (I) is displaced towards the right, hence the larger K_A is (or the smaller pK_A).

The base is stronger, the more firmly it binds protons, hence the more the equilibrium is displaced towards the left.

The constant K_A in fact defines the strength of the acid-base pair. The stronger the acid, the weaker the base.

Thus hydrocyanic acid HCN is a weak acid, $pK_A = 9.1$. CN^- is a fairly strong base. The ammonium ion NH_4^+ is an acid of the same strength: $pK_A = 9.2$. The corresponding base NH_3 has about the same strength as CN^-. Hydrofluoric acid HF, $pK_A = 3.2$ is stronger. F^- is a very weak base.

Acidity of an aqueous solution. pH

A solution is said to be more acid if the water in it has combined with more protons, i.e. if $|\ H_3O^+\ |$ is larger.

We have the equilibrium

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
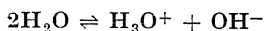
Applying the law of mass action

$$\frac{|\ OH^-\ |\ .\ |\ H_3O^+\ |}{|\ H_2O\ |^2} = K$$

K is fixed at a given temperature. The amount dissociated is always extremely small in relation to the total number of molecules of water in a dilute solution. $|\ H_2O\ |^2 = C^2_{H_2O}$ can thus be considered as practically constant, to all intents and purposes.

We thus have $|\ H_3O^+\ |\ .\ |\ OH^-\ | = K_{H_2O}$

The constant K_{H_2O} is very small: $10^{-13.98}$ at $25°$ C.

Temperature °C.										$pK_{H_2O} = -\log K_{H_2O}$
0	.	.	.	.	.	.	.	.	.	14·93
18	.	.	.	.	.	.	.	.	.	14·23
25	.	.	.	.	.	.	.	.	.	13·98
50	.	.	.	.	.	.	.	.	.	13·25
100	.	.	.	.	.	.	.	.	.	12·24

We thus see that at ordinary temperature $|\ H_3O^+\ |\ .\ |\ OH^-\ |$ is practically 10^{-14}. In pure water, there are as many H_3O^+ ions as OH^- ions, and so $|\ H_3O^+\ | = |\ OH^-\ | = 10^{-7}$.

A solution or medium is said to be acid if it contains an excess of H_3O^+ ions, $|\ H_3O^+\ | > 10^{-7}$. It is neutral when $|\ H_3O^+\ | = 10^{-7}$, and alkaline when $|\ H_3O^+\ | < 10^{-7}$.

Instead of using the activity of the H_3O^+ ions as a measure of the acidity of a solution, it is more convenient to use the function pH defined by the relation

$$pH = -\log_{10}|\ H_3O^+\ |$$

Thus the pH of pure water is 7. In acid solution the pH is < 7, right down to pH -1. In alkaline solution pH > 7, right up to pH 15.

Strong acids, strong bases; pH limits.—Some acids are very

strong, stronger than H_3O^+. They donate their protons quantitatively to the molecules of water to give H_3O^+. And, as there are 55 g.-mol of H_2O per litre, the acids disappear quantitatively in dilute solution. The equilibrium

$$\text{Acid} + H_2O \rightleftharpoons \text{Base} + H_3O^+$$
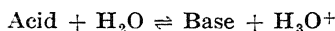
is displaced completely to the right. The scale of acidity is thus limited by the fact that the base H_2O is present in large quantities.

Acids stronger than H_3O^+ cannot exist in aqueous solution: HCl, HNO_3, $HClO_4$, are called 'strong acids'.

$$\text{HCl} + H_2O \rightarrow Cl^- + H_3O^+$$
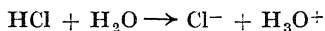
Cl^-, NO_3^-, ClO_4^-, are neutral from the point of view of acidity, for they cannot accept protons, and thus cannot react with molecules of water.

In the same way strong bases react quantitatively with water, considered as an acid:

$$\text{NaOH} + H_2O \rightarrow Na^+, H_2O + OH^-$$
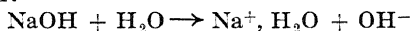
Na^+, K^+, Tl^+, etc., which correspond to strong bases, have no acid character, and they do not affect the pH of solutions.

SIMPLIFIED NOTATION.—The result of the action of water on the proton (hydration) has been symbolized as H_3O^+. For the sake of brevity, as already said for the other ions, we shall henceforth represent this entity as H^+ and we shall call the hydrated proton the hydrogen ion, as is the usual practice.

The equilibrium $\text{Acid} + H_2O \rightleftharpoons \text{Base} + H_3O^+$

will be written $\text{Acid} \rightleftharpoons \text{Base} + H^+$

The acidity constant for the acid-base pair will be written

$$\frac{|\text{ Base }|.|\text{ H}^+|}{|\text{ Acid }|} = K_A$$

NORMAL SOLUTIONS.—The term 'normal' is applied to a solution of an acid which is capable of liberating—if the dissociation is complete—1 g.-ion of hydrogen ions per litre. Thus, a normal solution of hydrochloric acid contains 1 g.-mol of HCl per litre. A normal solution of phosphoric acid contains $\frac{1}{3}$ of a gram-mol of phosphoric acid per litre, because, if its dissociation is complete, H_3PO_4 can liberate 3 hydrogen ions per molecule.

Normal basic solutions are defined in an analogous manner. A normal solution of sodium hydroxide contains 1 g.-mol of NaOH per litre.

We shall use the letter N to designate the normality, and the letter M to designate the concentration in gram-mols per litre. Thus an M solution of sulphuric acid contains 1 g.-mol per litre. It is twice normal, 2N.

IONIZATION OF SALTS.—Experience shows that in solution a considerable number of salts (particularly the salts of the alkali metals and the alkaline earth metals, as well as the perchlorates and the nitrates) behave like complexes of very low stability. They are practically completely ionized.

Thus sodium fluoride is completely ionized:

$$\text{NaF} \rightarrow F^- + Na^+$$
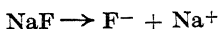
F^- is a base: Na^+ is a neutral ion from the point of view of the acidity (very weak acid).

In a similar manner ammonium chloride gives

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

NH_4^+ is an acid; Cl^- is a neutral ion (very weak base).

*p*H OF SOLUTIONS OF ACIDS, BASES, AND SALTS

General formulae for mixture of acid and the conjugate base

We have
$$\frac{|\,Base\,|.|\,H^+\,|}{|\,Acid\,|} = K_A$$

(1) Consider an acid of the form HA, such as hydrofluoric acid, which we shall introduce into the solution at a total concentration of c and the corresponding salt NaF which we shall introduce at the concentration c'; we have

$$NaF \longrightarrow Na^+ + F^-$$

Thus F^- and HF are the conjugate base and acid.

Let us calculate the *p*H of such a solution. We have the following relations:

$$\frac{|\,F^-\,|.|\,H^+\,|}{|\,HF\,|} = K_A$$

$$|\,Na^+\,| = c'; \quad |\,HF\,| + |\,F^-\,| = c + c'; \quad |\,H^+\,|.|\,OH^-\,| = K_{H_2O}$$

For the solution to remain electrically neutral we must have

$$|\,Na^+\,| + |\,H^+\,| = |\,OH^-\,| + |\,F^-\,|$$

We have thus 5 equations and 5 unknowns, whence

$$\boxed{|\,H^+\,| = K_A \frac{c - |\,H^+\,| + |\,OH^-\,|}{c' + |\,H^+\,| - |\,OH^-\,|}}$$

(2) If we take an acid which is a cation, for example NH_4^+, we obtain by mixing NH_4Cl at the concentration c with NH_3 at the concentration c':

$$\frac{|\,NH_3\,|.|\,H^+\,|}{|\,NH_4^+\,|} = K'_A$$

$$|\,Cl^-\,| = c; \quad |\,NH_4^+\,| + |\,NH_3\,| = c + c'; \quad |\,H^+\,|.|\,OH^-\,| = 10^{-14}$$

and
$$|\,NH_4^+\,| + |\,H^+\,| = |\,OH^-\,| + |\,Cl^-\,|$$

whence
$$|\,H^+\,| = K'_A \frac{c - |\,H^+\,| + |\,OH^-\,|}{c' + |\,H^+\,| - |\,OH^+\,|}$$

The same applies for the acids which are anions, such as HSO_4^-. A relation in $|\,H^+\,|^3$ is obtained which can be simplified by making certain approximations.

*p*H OF A SOLUTION OF AN ACID

In the general formula, $c' = 0$. We then have

$$|\,H^+\,| = K_A \frac{c - |\,H^+\,| + |\,OH^-\,|}{|\,H^+\,| - |\,OH^-\,|} \quad . \quad . \quad . \quad . \quad (I)$$

with $|H^+|.|OH^-| = 10^{-14.0}$. This formula permits $|H^+|$ to be obtained when K_A and c are known. **Flood's diagram** (fig. 6) presents these results in the form of $pH/ - \log c$ curves for different values of pK_A.

Below pH 6·5, $|OH^-|$ becomes negligible in relation to $|H^+|$ and we then have

$$|H^+|^2 = K_A(c - |H^+|) \quad . \quad . \quad . \quad . \quad . \quad \textbf{(II)}$$

We see that over a large region $|H^+|$ is negligible by comparison with c and we then have

$$|H^+|^2 = K_A.c . \quad . \quad . \quad . \quad . \quad . \quad \textbf{(III)}$$

or

$$\boxed{pH = \tfrac{1}{2}pK_A - \tfrac{1}{2}\log c}$$

This is the formula which we shall use in the majority of the cases. It corresponds to the FDC region of the diagram.

Formula **(II)** corresponds to fairly strong acids, region CABD of the diagram.

STRONG ACIDS.—When the acid is strong (completely dissociated), $|H^+|$ approaches c, $pH = -\log c$, which is the line AB of the diagram.

Examples.—(1) Consider a solution of hydrofluoric acid at the total concentration of 10^{-2}. Since $pK = 3.2$,

we have $\qquad\qquad pH = 1.6 + 1 = 2.6$

(2) In a solution of ammonium chloride we have

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

Cl^- is neutral; NH_4^+ is an acid of $pK = 9.2$

whence $\qquad\qquad pH = 4.6 - \tfrac{1}{2}\log c$

(3) pH of a molar solution of aluminium chloride. In water, aluminium ions are acids; they are in the form $Al(H_2O)^{3+}$ and $pK_A = 4.9$

$$pH = \tfrac{1}{2}4.9 = 2.45$$

The solution is at least as acid as a normal solution of acetic acid.

pH OF A SOLUTION OF A BASE.—In the general formula, in this case, $c = 0$ (upper part of Flood's diagram).

Making similar approximations as in the preceding cases: $|H^+|$ negligible in comparison with $|OH^-|$ and $|OH^-|$ negligible by comparison with c', a simplified formula applicable to the majority of cases is obtained:

$$\boxed{pH = 7 + \tfrac{1}{2}pK_A + \tfrac{1}{2}\log c'}$$

Strong bases.—$c' = |OH^-|$, whence $pH = 14 + \log c$.

Examples.—(1) pH of a normal solution of ammonia. Ammonia is a base in the equilibrium

$$NH_3 + H^+ \rightleftharpoons NH_4^+; \quad pK = 9.2$$

whence $\qquad\qquad pH = 7 + 4.6 = 11.6$

(2) pH of potassium cyanide in M/10 solution.

KCN is completely dissociated.

$$KCN \longrightarrow CN^- + K^+$$

K^+ is a neutral ion from the point of view of acidity.

CN^- is a base:

$$CN^- + H^+ \rightleftharpoons HCN; \quad pK = 9\cdot1$$

whence $\quad\quad\quad\quad pH = 7 + 4\cdot55 - 0\cdot5 = 11\cdot05$

Basicity constant.—When a base is dissolved in water the equilibrium:

$$\text{Base} + H_2O \rightleftharpoons \text{Acid} + OH^-$$
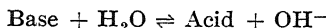
is set up with $\quad\quad\quad \dfrac{|\text{ Acid }|.|\text{ OH}^-|}{|\text{ Base }|} = K_B$

This is the basicity constant.

Thus, with ammonia, we have

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
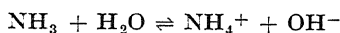
with $\quad\quad\quad\quad \dfrac{|\text{ NH}_4^+|.|\text{ OH}^-|}{|\text{ NH}_3|} = K_B$

or $\quad\quad\quad\quad\quad \dfrac{|\text{ Base }|.|\text{ H}^+|}{|\text{ Acid }|} = K_A$

whence $\quad\quad\quad K_A.K_B = |\text{ H}^+|.|\text{ OH}^-| = 10^{-14}$

Either K_A or K_B can be used in these formulae. For reasons of simplicity we shall utilize K_A.

pH OF A MIXTURE OF CONJUGATE ACID AND BASE.—

In the general formula, we can usually neglect $|\text{ H}^+|$ and $|\text{ OH}^-|$ in comparison with c and c'. We then have

$$pH = pK_A + \log \frac{C'}{C} \quad \text{or} \quad pH = pK_A + \log \frac{C_{\text{Base}}}{C_{\text{Acid}}}$$

If $C_{\text{Base}} = C_{\text{Acid}}$ then $pH = pK_A$.

BUFFER SOLUTIONS.—The term 'buffer' is applied to a solution into which H^+ ions can be introduced or from which they can be withdrawn, by addition of acids and bases, without notably changing the pH. This is the case with a solution containing conjugate acids and bases. For example, a buffer solution can be made up by mixing an acid with one of its completely ionized salts: for example, acetic acid, sodium acetate, we then have the acid, acetic acid, and the conjugate base, the acetate ion. A base can also be mixed with one of its salts with a strong acid, this salt being completely ionized: ammonia, ammonium chloride. We then have the acid, ammonium ion, and the conjugate base, ammonia.

In effect, the ratio base/acid can be considerably varied without changing the pH very much. pH is in fact a function of the form $y = a + \log x/(b - x)$ (fig. 5).

Examples.—(1) Consider a mixture of acetic acid + sodium acetate. We have

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$
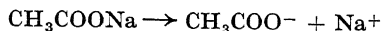
Na^+ is neutral; $CH_3CO_2^-$ is the conjugate base to acetic acid, $pK = 4\cdot8$, and we have

$$pH = 4\cdot8 + \log \frac{C_{CH_3CO_2^-}}{C_{CH_3CO_2H}}$$

Suppose that the two concentrations are both equal to 1, then the $pH = 4.8$. If a strong acid be added to the solution at a concentration $0.1N$, we shall have

$$C_{CH_3CO_2^-} = 1 - 0.1, \quad C_{CH_3CO_2H} = 1 + 0.1, \quad \text{and} \quad pH = 4.8 + \log\frac{0.9}{1.1} = 4.7$$

The pH has thus only changed a little; the addition of an acid up to a concentration which should be $0.1N$ has only changed the pH from 4.8 to 4.7. In pure water, the pH would change from 7 to 1.

(2) Consider the mixture ammonia/ammonium chloride. We have

$$NH_4^+ \rightleftharpoons NH_3 + H^+; \quad pK = 9.2$$
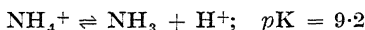
Thus the pH of the buffer solution containing equimolecular proportions of ammonium chloride and ammonia is 9.2.
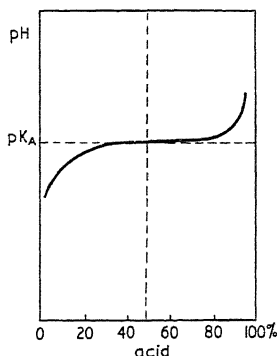
FIG. 5.—$pH = pK + \log\dfrac{|\text{ Base }|}{|\text{ Acid }|}$

(3) The solution of two salts of the same acid constitutes a mixture of an acid and its conjugate base: this is also a buffer solution.

Taking the case of the mixture monosodium phosphate/disodium phosphate,

$$NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$$
$$Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{2-}$$

and $\quad\underset{\text{Acid}}{H_2PO_4^-} \rightleftharpoons \underset{\text{Base}}{HPO_4^{2-}} + H^+$
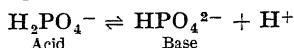
to a first approximation

$$pH = 7.2 + \log\frac{C_{Na_2HPO_4}}{C_{NaH_2PO_4}}$$

Experiment.—Add normal hydrochloric acid to a molar solution of sodium acetate, and follow the curve of fig. 5. At the start the pH is 9.4, phenolphthalein is red. It is very rapidly decolorized, pH 8–9. A drop of bromocresol green is then added (yellow pH 3.8—blue pH 5.4). As soon as the level portion of the curve is reached, the pH changes very little, and the indicator is coloured green.

On the contrary, in distilled water, pH 5·5–5·0 as CO_2 is present, a drop of acid will immediately cause the indicator to change colour.

Use of buffer solutions.—Buffer solutions play an important role in qualitative analysis. They are used for keeping the pH of a solution fixed at a known value in order to carry out either a precipitation or an oxidation, or sometimes to form a complex. They introduce considerable amounts of ions into the solution; the ionic strength of the solution must be borne in mind.

The buffer solutions most commonly used in analysis are the following:

	pH		pH
N-HCl (H_3O^+/H_2O)	0	M-NH_4Cl + M-NH_3	9·2
0·1N-HCl	1	$NaHCO_3$ saturated + M-Na_2CO_3	
0·01N-HCl	2	(measured)	9·4
M-$CH_2ClCO_2^-$ + M-CH_2ClCO_2H	2·9	M/4-Borax (measured)	9·3
M-$CH_3CO_2^-$ + M-CH_3CO_2H	4·8	0·01N-NaOH (H_2O/OH^-)	12
M-hexamine + M-hexamine		0·1N-NaOH	13
hydrochloride	5·0	N-NaOH	14
$NaHCO_3$ satd. + CO_2 (measured)	7·4		

EFFECT OF THE CONCENTRATION, DILUTION OF ACIDS AND BASES

It is convenient to define the degree of dissociation

$$\alpha = \frac{\text{number of dissociated molecules (or ions)}}{\text{total number of ions or molecules}}$$

For an acid in solution in water, we have

$$\frac{|\text{ Base }|\cdot|\text{ H}^+|}{|\text{ Acid }|} = K_A$$

If c is the total concentration of the acid, then it can easily be seen that

$$\frac{\alpha^2 \cdot c}{1 - \alpha} = K_A$$

whence

$$\frac{\alpha^2}{1 - \alpha} = \frac{K_A}{c}$$

It is seen that the degree of dissociation of the acid depends solely on K_A/c. It can be seen that if K_A is given, then as the solution is diluted, c decreases and so K_A/c increases, and as a result α increases. If the dilution is carried far enough, the acid dissociates completely; it then behaves like a strong acid.

K_A/c	c (per cent)	K_A/c	c (per cent)
$< 10^{-4}$	< 1 very weak acids	10	90
10^{-4}	1	10^2	99
10^{-2}	10	$> 10^3$	$> 99·9$ 'strong' acids
0·5	50		

Similar remarks can be made about basic solutions.

These results are made clear on Flood's diagram.

Flood's diagram (fig. 6).—This diagram enables one to find the pH of various solutions as a function of c and of pK_A no matter what the concentration.

It is also possible to determine from the graph the pH of buffer solutions and of acid-base mixtures, including the cases where the simple formulae cease to apply. (See H. Flood, *Z. Elektrochem*, 1940, **46**, 668.)
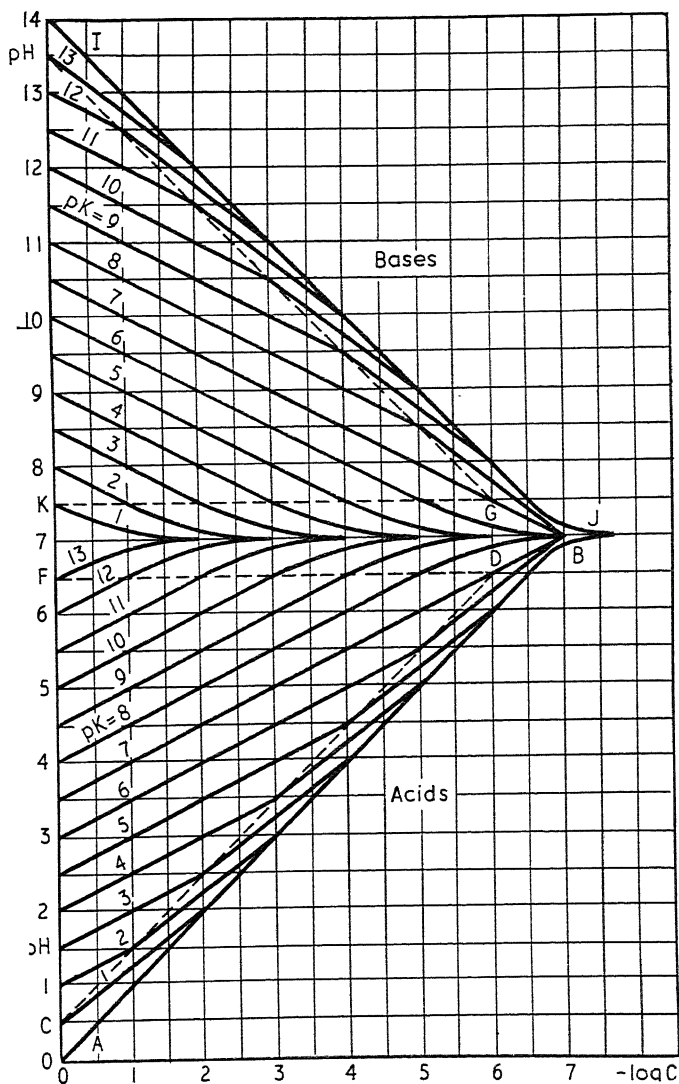
FIG. 6.—FLOOD'S DIAGRAM

pH of a mixture of two acid-base systems.—In the systems Acid$_1$-Base$_1$ and Acid$_2$-Base$_2$, the equilibrium

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1 \quad . \quad . \quad . \quad . \quad (I)$$

is set up, and also the equilibria:

$$Acid_1 \rightleftharpoons Base_1 + H^+ \quad . \quad . \quad . \quad . \quad . \quad \text{(III)}$$

$$Acid_2 \rightleftharpoons Base_2 + H^+ \quad . \quad . \quad . \quad . \quad . \quad \text{(IV)}$$

with $\dfrac{|\, Base_1\,|\cdot|\, H^+\,|}{|\, Acid_1\,|} = K_1$ and $\dfrac{|\, Base_2\,|\cdot|\, H^+\,|}{|\, Acid_2\,|} = K_2$. (II)

Thus in a mixture of acetic acid and ammonium acetate the following equilibrium is set up:

$$CH_3CO_2H + NH_3 \rightleftharpoons CH_3CO_2^- + NH_4^+$$

(1) Suppose that equivalent quantities of an acid of one system with the base of the other are mixed. In this particular case, we have

$$|\, Acid_1\,| + |\, Base_2\,| \rightleftharpoons |\, Acid_2\,| + |\, Base_1\,|$$

Thus, from (I) as much of $Base_1$ as of $Acid_2$ is produced, so that, neglecting the quantities of $Base_1$ and of $Acid_2$ produced by the water, i.e. when the strengths of the acids and bases and their concentrations are sufficiently large, we obtain the relation:

$$|\, Base_1\,| = |\, Acid_2\,| \quad \text{whence} \quad |\, Acid_1\,| = |\, Base_2\,|$$

the relations (II) above then give

$$\frac{|\, Base_1\,|\cdot|\, Base_2\,|}{|\, Acid_1\,|\cdot|\, Acid_2\,|} \cdot |\, H^+\,|^2 = K_1 K_2$$

whence $|\, H^+\,|^2 = K_1 K_2$

and $\boxed{p\mathrm{H} = \tfrac{1}{2}p\mathrm{K}_1 + \tfrac{1}{2}p\mathrm{K}_2}$

The pH is thus in principle independent of the concentration.

(2) When the proportions of $Acid_1$ and $Base_2$ are not equivalent to one another, the final pH is little different from that given by the formula. Thus for

$$|\, Acid_1\,| = m\,|\, Base_2\,|$$

we have $p\mathrm{H} = \tfrac{1}{2}p\mathrm{K}_1 + \tfrac{1}{2}p\mathrm{K}_2 - \tfrac{1}{2}\log m$

The pH changes considerably when the orders of magnitude become different.

Applications.—(1) p*H of a salt solution.*—Take, for example, a solution of ammonium acetate $CH_3CO_2NH_4$. It is ionized:

$$CH_3CO_2NH_4 \rightarrow CH_3CO_2^- + NH_4^+$$

and so $NH_4^+ + CH_3CO_2^- \rightleftharpoons CH_3CO_2H + NH_3$

The pH of this solution is the same as that of a solution into which the acid CH_3CO_2H, $p\mathrm{K}_1 = 4\cdot8$, and the base NH_3, $p\mathrm{K}_2 = 9\cdot2$, are introduced in equivalent proportions.

$$p\mathrm{H} = \tfrac{1}{2}9\cdot2 + \tfrac{1}{2}4\cdot8 = 7\cdot0$$

(2) *Mixture of salts with acids or bases.*—Consider a mixture of equi-molecular quantities of acetic acid and of sodium fluoride. This is a mixture of the acid CH_3CO_2H and the base F^-.

$$NaF \rightarrow F^- + Na^+; \quad p\mathrm{K}_1 = 3\cdot2; \quad p\mathrm{K}_2 = 4\cdot8; \quad p\mathrm{H} = \tfrac{1}{2}(3\cdot2 + 4\cdot8) = 4\cdot0$$

For a mixture of equimolecular quantities of ammonium chloride and of potassium cyanide, we have

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \quad . \quad . \quad . \quad . \quad pK_1 = 9.2$$
$$KCN \rightarrow K^+ + CN^- \quad . \quad . \quad . \quad . \quad pK_2 = 9.1$$

This is a mixture of the acid NH_4^+ and the base CN^-:

$$pH = \tfrac{1}{2}(9.2 + 9.1) = 9.15.$$

Polyacids, ampholytes, disproportionation.—Polyacids are able to give up several protons in succession. Thus carbonic acid:

$$\left.\begin{array}{l} H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \quad pk_2 \\ HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad pk_1 \end{array}\right\}* \quad . \quad . \quad . \quad \text{(I)}$$

or the cation M^+

$$\left.\begin{array}{l} M^+,H_2O \rightleftharpoons MOH + H^+ \\ MOH \rightleftharpoons MO^- + H^+ \end{array}\right\} . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

or again, the ammonium ion:

$$\left.\begin{array}{l} NH_4^+ \rightleftharpoons NH_3 + H^+ \quad pk_4 \\ NH_3 \rightleftharpoons NH_2^- + H^+ \quad pk_3 \end{array}\right\} \quad . \quad . \quad . \quad \text{(III)}$$

It is evidently easier to give up the first proton than the second. H_2CO_3 is thus a stronger acid than HCO_3^- and $pk_2 \leqslant pk_1$.

When the solution is made acid, the equilibria (I) above are displaced towards the left. There are thus obtained in succession, in going from an alkaline solution towards an acid one, the species: CO_3^{2-}, HCO_3^-, H_2CO_3. Similarly, we have in an alkaline solution the anion MO^-, then MOH, and finally the cation M^+ in acid solutions. The same remarks apply to the series NH_2^-, NH_3, NH_4^+.

Compounds like HCO_3^- and MOH sometimes behave as acids, and sometimes as bases. To them the term 'ampholyte' is applied.

The preceding equilibria can, for example, be represented as

$$2HCO_3^- \rightleftharpoons CO_3^{2-} + H_2CO_3$$

This is the disproportionation equilibrium, and we have

$$\frac{|\,CO_3^{2-}\,|.|\,H_2CO_3\,|}{|\,HCO_3^-\,|^2} = K = \frac{k_1}{k_2}$$

Since $k_2 > k_1$, HCO_3^- is present in perceptible quantity in the solution. We shall see that, by the disappearance of CO_3^{2-}, or of H_2CO_3, the equilibrium can be displaced towards the right. HCO_3^- then disproportionates. It can cease to exist under certain conditions.

pH of a solution of an ampholyte.—HCO_3^- is the acid of a system with pk_1 and the base of the other system of pk_2. Since the concentrations in the two systems are evidently the same:

$$pH = \tfrac{1}{2}(pk_1 + pk_2)$$

and the pH is independent of the concentration.

In this particular case $pH = \tfrac{1}{2}(6.4 + 10.2) = 8.3$.

---

* Small k's are used to represent 'partial' dissociation constants corresponding to individual stages of the dissociation of an acid capable of donating more than one H^+ ion, etc.

4

Summary of simplified formulae

Solution of an acid	$pH = \frac{1}{2}pK_A - \frac{1}{2}\log C$
,, ,, a base	$pH = 7 + \frac{1}{2}pK_A + \frac{1}{2}\log C$
,, ,, ,, salt $(Acid_1 + Base_2)$ . .	$pH = \frac{1}{2}pK_1 + \frac{1}{2}pK_2$
Buffer solution $(Acid_1 + Base_1)$ . . .	$pH = pK + \log\dfrac{|\,Base\,|}{|\,Acid\,|}$
Basicity constant	$K_A . K_B = K_{H_2O}$

Constants of common acid-base pairs in water

Name of the Acid	Formula of Acid	Formula of Base	pK
Hydronium ion	H_3O^+	H_2O	
Pyrophosphoric acid	$H_4P_2O_7$	$H_3P_2O_7^-$	0·85
Oxalic acid	$H_2C_2O_4$	$HC_2O_4^-$	1·2
Dichloroacetic acid	$Cl_2CHCOOH$	Cl_2CHCOO^-	1·3
Phosphorous acid	H_3PO_3	$H_2PO_3^-$	1·5–1·8
Hypophosphorous acid	H_3PO_2	$H_2PO_2^-$	1–2
Sulphurous acid	H_2SO_3	HSO_3^-	1·8
Bisulphate ion	HSO_4^-	SO_4^{2-}	1·9 (1·05)
Pyrophosphate ion	$H_3P_2O_7^-$	$H_2P_2O_7^{2-}$	2·0
Orthophosphoric acid	H_3PO_4	$H_2PO_4^-$	2·1–2·2
Arsenic acid	H_3AsO_4	$H_2AsO_4^-$	2·3
Monochloroacetic acid	$ClCH_2COOH$	$ClCH_2COO^-$	2·9
Hydrofluoric acid	HF	F^-	3·2
Nitrous acid	HNO_2	NO_2^-	3·4
Formic acid	$HCOOH$	$HCOO^-$	3·7
Cyanic acid	$HCNO$	CNO^-	3·8
Bioxalate ion	$HC_2O_4^-$	$C_2O_4^{2-}$	4·1
Benzoic acid	C_6H_5COOH	$C_6H_5COO^-$	4·2
Anilinium ion	$C_6H_5NH_3^+$	$C_6H_5NH_2$	4·6
Hydrazoic acid	HN_3	N_3^-	4·7
Acetic acid	CH_3COOH	CH_3COO^-	4·8
Aluminium ion	$Al^{3+},aq.$	$AlOH^{2+},aq.$	4·9
Hexamethylenetetramine ion . .	$(CH_2)_6N_4H^+$	$(CH_2)_6N_4$	4·9
Pyridonium ion	$C_5H_5NH^+$	C_5H_5N	5·15
Bisulphite ion	HSO_3^-	SO_3^{2-}	5·3–7·1
Hydroxylaminium ion	NH_3OH^+	NH_2OH	6·0
Carbon dioxide	$CO_2,aq.$	HCO_3^-	6·4
Pyrophosphate ion	$H_2P_2O_7^{2-}$	$HP_2O_7^{3-}$	6·7
Phosphite ion	$H_2PO_3^-$	HPO_3^{2-}	6·2–6·6
Arsenate ion	$H_2AsO_4^-$	$HAsO_4^{2-}$	4·4–6·8
Bichromate ion	$HCrO_4^-$	CrO_4^{2-}	6·4
Hydrosulphurous acid	H_2S	HS^-	7·1
Phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	7·2
Hypochlorous acid	$HClO$	ClO^-	7·2–7·5
Hydrocyanic acid	HCN	CN^-	9·1
Arsenate ion	$HAsO_4^{2-}$	AsO_4^{3-}	9·2–12·0
Arsenious acid	$HAsO_2$	AsO_2^-	9·2
Ammonium ion	NH_4^+	NH_3	9·2
Boric acid	HBO_2	BO_2^-	9·2
Pyrophosphate ion	$HP_2O_7^{3-}$	$P_2O_7^{4-}$	9·6
Bicarbonate ion	HCO_3^-	CO_3^{2-}	10·2
Phosphate ion	HPO_4^{2-}	PO_4^{3-}	12·3
Hypoiodous acid	HIO	IO^-	10·0–12·2
Calcium ion	Ca^{2+}	$CaOH^+$	12·6
Bisulphide ion	HS^-	S^{2-}	11·9–14·9
Water	H_2O	OH^-	
Hydroxyl ion	OH^-	O^{2-}	

Notes.—The acids are placed in this table in the order of decreasing, and the bases in the order of increasing, strength.

Hydriodic, perchloric, hydrobromic, hydrochloric, nitric, chromic (pk_2) and sulphuric acids (pk_2) are strong, placed here in the order of decreasing strength.

Potassium and sodium hydroxides are strong bases.

An acid can react with all bases placed below it in the table. In quantitative analysis we shall see that to get practically complete reaction there must be a difference of pK of 5·4 units.

Bases conjugate with strong and fairly strong acids (top of table) are weakly basic and vice versa.

In principle, pK's are calculated from activities.

The values given here can only be used in aqueous solution.

APPARENT pK VALUES

pK values given here are those corresponding to the use of concentrations instead of activities. Their value is given here as a function of the ionic strength I.

$\sqrt{I}$:	0	0·25	0·5
HR$^+$ — R			
$\overline{NH_4^+}$ — NH_3 . . .	9·25	9·3	9·35
HR — R$^-$			
$\overline{H_3PO_4}$ — $H_2PO_4^-$ . .	2·10	2·0	1·85
HR$^-$ — R^{2-}			
$\overline{H_2PO_4^-}$ — HPO_4^{2-} . .	7·2	6·85	6·60
HR^{2-} — R^{3-}			
$\overline{HPO_4^{2-}}$ — PO_4^{3-} . .	12·65	12·1	11·75

APPLICATIONS

(1) **Neutralization of an acid.**—Consider the neutralization of acetic acid by caustic soda. Initially the solution is acid, then we get a solution containing both the acid CH_3CO_2H and its corresponding base $CH_3CO_2^-$. At the completion of the neutralization there is only the base $CH_3CO_2^-$.

(2) **Neutralization of 00·1M carbonic acid.**

$$pk_2 = 6·4; \quad pk_1 = 10·2$$

At the start, the solution is acid.

$$pH = \tfrac{1}{2}pK + \tfrac{1}{2} \log C = 3·2 + 1 = 4·2$$

The addition of caustic soda causes HCO_3^- to be formed, and the solution then contains the acid H_2CO_3 and the base HCO_3^-, $pK_A = 6·4$. This is a buffer solution and we have

$$pH = pK + \log \frac{|\ HCO_3^-\ |}{|\ H_2CO_3\ |}$$

For 0·5NaOH and 1H$_2$CO$_3$, we have $pH = pk_2$ of 6·4.

For 1NaOH and 1H$_2$CO$_3$ the solution contains the 'acid salt' HCO$_3^-$ which can play the part of both an acid and a base:

$$pH = \tfrac{1}{2}pk_1 + \tfrac{1}{2}pk_2 = 8\cdot3$$

At 1·5NaOH we have HCO$_3^-$ + CO$_3^{2-}$ and $pH = pk_1 = 10\cdot2$.

At 2·0NaOH we have CO$_3^{2-}$ and $pH = 7 + \tfrac{1}{2}pk_1 + \tfrac{1}{2}\log C = 11\cdot1$.

(3) **Mixtures of acids.**—Consider a mixture of formic acid with $pk_1 = 3\cdot7$, and ammonium chloride, $pk_2 = 9\cdot2$. Neutralization takes place as in the case of polyacid:

$$HCO_2H + NH_4^+; \quad pH = \tfrac{1}{2}pk_1 - \tfrac{1}{2}\log C$$
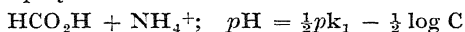
In effect the concentration of the ions H$_3$O$^+$ due to NH$_4^+$ is negligible compared to that which is due to HCOOH.

We thus obtain the buffer solution HCO$_2$H + HCO$_2^-$, $pH = pk_1$, when half the formic acid is neutralized.

When all the formic acid is neutralized, HCO$_2^-$ and NH$_4^+$ are present, constituting a mixture of an acid and a base of two different systems. Supposing that the concentrations are equal, we have

$$pH = \tfrac{1}{2}pk_1 + \tfrac{1}{2}pk_2$$

NH$_4^+$ is then neutralized giving the base NH$_3$; a buffer mixture with $pH = pk_2$.

When all the NH$_4^+$ is neutralized, we have a mixture of two bases HCO$_2^-$ and NH$_3$. The stronger base determines the pH:

$$pH = 7 + \tfrac{1}{2}pk_2 + \tfrac{1}{2}\log C$$

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COMPLEXES (EXCHANGES OF IONS AND POLAR MOLECULES)

DEFINITIONS.—A complex can give up a 'particle': it is the donor of this particle, and as a result the following equilibrium is set up:

$$\text{Donor} \rightleftharpoons \text{acceptor} + p$$
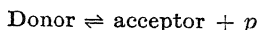
denoting by p the particle under consideration.

Example.—The ion $FeCNS^{2+}$ can give up $\boxed{CNS^-}$:

$$FeCNS^{2+},\text{aq.} \rightleftharpoons Fe^{3+},\text{aq.} + \boxed{CNS^-}$$
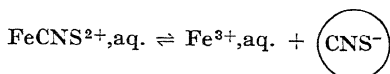
Mercuric chloride is a complex which can donate the particle $\boxed{Cl^-}$:

$$HgCl_2,\text{aq.} \rightleftharpoons HgCl^+,\text{aq.} + \boxed{Cl^-}$$
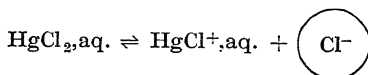
The silver ammine complex can donate $\boxed{NH_3}$:

$$AgNH_3^+,\text{aq.} \rightleftharpoons Ag^+,\text{aq.} + \boxed{NH_3}$$
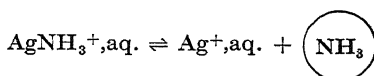
Generalization of the properties of acids and bases.—Acids are complexes with the particle $\boxed{H^+}$. In this chapter the very numerous complexes with other particles will be studied. The general properties, the methods of reasoning, and the formulae are analogous to those met with in the discussion of acids and bases. We shall summarize them as follows:

ION EXCHANGE REACTIONS

The particles are unable to exist in the free state and in order for a donor, $Donor_1$, to donate a particle an acceptor, $Acceptor_2$, must be present. We thus get:

$$\begin{array}{c} Donor_1 - p \rightleftharpoons Acceptor_1 \\ Acceptor_2 + p \rightleftharpoons Donor_2 \\ \hline Donor_1 + Acceptor_2 \rightleftharpoons Acceptor_1 + Donor_2 \end{array}$$

Example.—Exchange of CNS⁻

$$Hg(CNS)_3^- \rightleftharpoons Hg(CNS)_2 + CNS^-$$

$$Fe^{3+}, aq. + CNS^- \rightleftharpoons FeCNS^{2+}$$
$$\overline{Hg(CNS)_3^- + Fe^{3+}, aq.} \rightleftharpoons \overline{FeCNS^{2+} + Hg(CNS)_2}$$

AQUEOUS SOLUTIONS. HYDROLYSIS. COMPLEXES WITH THE IONS OF WATER

Water probably plays the part of an acceptor relative to all charged particles, polar or polarized.

Example.—Thus if mercuric chloride, which can donate Cl^-, is introduced into water, we have

$$HgCl_2 \rightleftharpoons HgCl^+ + Cl^-$$

and the water combines with the Cl^-:

$$mH_2O + Cl^- \rightleftharpoons Cl(H_2O)_m^-$$

so that the dissolution of $HgCl_2$ corresponds to the reaction

$$HgCl_2 + mH_2O \rightleftharpoons HgCl^+ + Cl(H_2O)_m^-$$

Hydrolysis, or hydration of the particle, causes the ionization of the complex.

But, unlike the proton, water cannot in general donate itself. It can donate only H^+, OH^-, or O^{2-}. Complexes with the ions of water are then obtained (see p. 50).

SIMPLIFIED NOTATION.—In solution, $HgCl^+$ as well as Cl^- is hydrated, and no doubt also $HgCl_2$. As in the last chapter, when dealing with acids and bases, we shall omit the particle H_2O in the equations, it being well understood that the particle Cl^- in the free state must not be confused with the hydrated ion in solution. We thus obtain

$$HgCl_2 \rightleftharpoons HgCl^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$

with

$$\frac{|\,HgCl^+\,|.|\,Cl^-\,|}{|\,HgCl_2\,|} = K_c \quad . \quad . \quad . \quad . \quad \text{(II)}$$

and
$$| \text{Cl}^- | = \text{K}_c \frac{| \text{HgCl}_2 |}{| \text{HgCl}^+ |}$$

Using the more convenient expression $p\text{Cl}^- = - \log | \text{Cl}^- |$, this becomes

$$p\text{Cl}^- = p\text{K}_c + \log \frac{| \text{HgCl}^+ |}{| \text{HgCl}_2 |}$$

or generally

$$p\text{X} = p\text{K}_c + \log \frac{| \text{Acceptor} |}{| \text{Donor} |}$$

Special case.—The particle is $\boxed{\text{H}^+}$:

$$p\text{H} = p\text{K}_\text{A} + \log \frac{| \text{Base} |}{| \text{Acid} |}$$

Strength of donors and acceptors. Stability of complexes.— In the equilibrium (I), the larger $| \text{Cl}^- |$, the stronger is the donor HgCl_2, and consequently the weaker the acceptor HgCl^+, and vice versa.

In the equation (II), the strength of the donor and the acceptor is defined by the constant K_c. The larger K_c, or the smaller $p\text{K}_c$, the stronger the donor.

Thus it is $p\text{K}_c$ which gives us a measure of the strength of acceptor-donor pairs. $p\text{Cl}^-$ expresses the state of the solution.

If a donor is strong, we say that the complex is of low stability, and easily donates its particles. K_c is called the stability constant of the complex. The smaller K_c, or the larger $p\text{K}_c$, the more stable the complex.

Examples.—The hypochlorous anion ClO^- is a weak donor of O^{2-}:

$$\text{ClO}^- \rightleftharpoons \text{Cl}^+ + \text{O}^{2-}$$
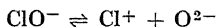
Cl^+ is a strong acceptor of O^{2-}. ClO^- is a very stable complex with O^{2-}.

NaNO_3 is a very strong donor of Na^+, and is a very unstable complex with Na^+.

$$\text{NaNO}_3 \rightarrow \text{NO}_3^- + \text{Na}^+$$

Thus NO_3^- is a very weak acceptor of Na^+.

On the other hand, NO_3^- is a very stable complex with O^{2-}; N^{5+} cannot be very easily obtained, because it is too strong an acceptor.

Constants of complexes.—In order to be able to predict reactions, it is necessary to have a table of the different constants for each particle, Cl^-, NO_3^-, Al^{3+}, NH_3, etc. Our knowledge in this field is extremely limited, since we know very little about complexes in solution, and know only a small number of constants. We shall give a certain number of these in the second part of this volume.

Example.—Exchange of $\boxed{\text{CNS}^-}$

Donor	Acceptor	pk
Hg(CNS)_4^{2-}	Hg(CNS)_3^-	0·6
Hg(CNS)_3^-	Hg(CNS)_2	1·7
FeCNS^{2+}	Fe^{3+}	2·3
Hg(CNS)_2	HgCNS^+ $\left.\rule{0pt}{2.5ex}\right\}$	$p\text{k}_1 + p\text{k}_2 = 19\cdot7$
HgCNS^+	$\text{Hg}^{2+},\text{aq.}$	

The same remarks can be made as about the exchange of protons: the strongest donors are those at the top of the table (weakest, most unstable complexes), and consequently these are also the weakest acceptors.

An acceptor can react with a donor situated below it in the table. Thus

$$Hg(CNS)_3{}^- + Fe^{3+} \rightleftharpoons Hg(CNS)_2 + Fe(CNS)^{2+}$$
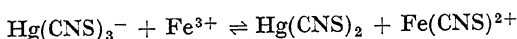
We shall see in quantitative analysis that, for a reaction to be practically quantitative (99·8 per cent), a difference of 5·4 pK units is necessary.

KCN is a very unstable complex which does not exist in water.

Characteristic concentration in different solutions.—The lines of argument are fairly similar to those already employed relative to the proton exchange. Consider for example a system involving F^-:

$$\underset{\text{Donor}}{AlF^{2+}} \rightleftharpoons \underset{\text{Acceptor}}{Al^{3+}} + F^-$$
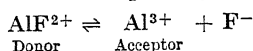
For the sake of simplicity we shall suppose that there are no other complexes than AlF^{2+} between Al^{3+} and F^-.

Let c be the total concentration of AlF^{2+} introduced into solution (e.g. as $AlClF_2$) and c' the total concentration of aluminium chloride added. We have the following equations:

$$\frac{|\,Al^{3+}\,|\,.\,|\,F^-\,|}{|\,AlF^{2+}\,|} = K$$

Total concentration of Al:

$$c + c' = |\,AlF^{2+}\,| + |\,Al^{3+}\,|$$

Total concentration of F:

$$c = |\,AlF^{2+}\,| + |\,F^-\,|$$

whence

$$|\,F^-\,| = K\frac{c - |\,F^-\,|}{c' + |\,F^-\,|}$$

Simplified formulae.—If the complex is so stable at the concentration given that F^- becomes negligible in comparison with c and c', we have

$$|\,F^-\,| = Kc/c'$$

(1) *Buffer solution for F^-.*—The conjugated donor and acceptor AlF^{2+} and Al^{3+} are introduced into solution at the same time. Then

$$pF^- = pK + \log\frac{|\,\text{Acceptor}\,|}{|\,\text{Donor}\,|} = pK + \log c/c'$$

i.e. a formula analogous to that obtained for the pH of a mixture of conjugate acid and base.

The mixture is a buffer solution for F^-. If F^- be added or withdrawn from this solution, the value of pF^- changes very little. The pF^- of the solution can thus be fixed in the neighbourhood of $pF^- = pK$.

(2) *Solution of the complex AlF^{2+}.*—

$$c' = 0, \quad \text{whence} \quad pF^- = \tfrac{1}{2}pK - \tfrac{1}{2}\log c$$

a formula analogous to that for the pH of an acid.

(3) *Solution of Al^{3+}.*—$|\,F^-\,| = 0$, since here the solvent cannot provide any exchangeable particle.

(4) *Mixture of two systems.*—Consider the systems

$$AlF^{2+} \rightleftharpoons Al^{3+} + F^- \quad . \quad . \quad . \quad K_1$$
$$FeF^{2+} \rightleftharpoons Fe^{3+} + F^- \quad . \quad . \quad . \quad K_2$$
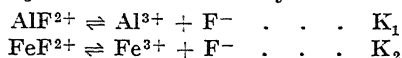
which both involve the particle F^-.

If the acceptor of one of the systems, Fe^{3+}, is mixed with the donor, AlF^{2+}, of the other, we have

$$AlF^{2+} + Fe^{3+} \longrightarrow Al^{3+} + FeF^{2+} \quad \text{with} \quad |Al^{3+}| = |FeF^{2+}|$$
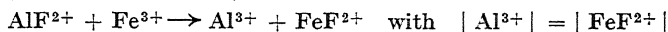
If AlF^{2+} and Fe^{3+} be mixed in equivalent proportions, $|AlF^{2+}| = |Fe^{3+}|$ whence

$$pF^- = \tfrac{1}{2}(pK_1 + pK_2)$$

This is a formula analogous to that for the pH of an acid-base mixture.

Experiment. Buffer solutions of CNS^-.—We know that the concentration of CNS^- can be directly revealed by the addition of a little Fe^{3+}; the red coloration of $Fe(CNS)^{2+}$ is the more intense, the greater the concentration of CNS^-.

A mixture of CNS^- with $Hg(II)$ in excess, constitutes a buffer mixture of $Hg^{2+}/HgCNS^+$. We have

$$p\text{CNS}^- = pK + \log \frac{|Hg^{2+}|}{|HgCNS^+|}$$

If a drop of a dilute solution of ferric iron be added to this solution, a coloration due to the presence of free CNS^- in the solution is obtained.

If now dilute thiocyanate be added to this solution, the value of pCNS$^-$ changes very little, and consequently the red coloration does not alter in intensity.

A parallel experiment can be made with a solution containing the same quantity of Fe^{3+}, to which the same quantities of CNS^- are added. In this unbuffered solution, $|CNS^-|$ varies rapidly, and as a result the red coloration changes rapidly as well.

CHEMICAL PROPERTIES OF COMPLEXES, SEQUESTERING (OR MASKING)

Complexes are separate chemical entities and their properties are different from those of their components. The following types can be distinguished:

(1) **Perfect complexes.**—They are very stable and practically do not liberate particles (non-electrovalent bonds). Examples are: $FeCN_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Au(CN)_2^-$, NO_3^-, SO_4^{2-}, etc.

Thus in the ion $Fe(CN)_6^{4-}$, Fe^{2+} cannot be detected, the ferrous ion is completely sequestered.

But they can be destroyed by variations of temperature, pH, etc.

(2) **General case.**—The majority of complexes react with water to liberate, to some extent, their constituents in the ionized form as we have already seen. Thus

$$FeF^{2+} \rightleftharpoons Fe^{3+} + F^-$$
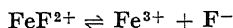
The ion Fe^{3+} here is partially sequestered.

Formulae which give $p\text{Fe}^{3+}$ or $p\text{F}^-$ can be applied, and in this way the properties of their aqueous solutions may be forecast. These solutions contain at one and the same time the constituent ions and those of the complex.

(3) **Very unstable complexes.**—The complexes with Na^+, K^+, NH_4^+, scarcely exist in water. Those with ClO_4^-, NO_3^-, Ca^{2+}, Mg^{2+}, are in general fairly unstable. Their solutions have the properties of the constituent ions. SO_4^{2-}, Cl^-, give various complexes with the majority of cations. They are in general rather unstable.

Influence of excess of reagent.—Take for example the case of ferric iron Fe^{3+}, to which a little F^- has been added. The complex fluoride of ferric iron FeF^{2+} is obtained, and we have

$$\mid Fe^{3+} \mid \; = K \frac{\mid FeF^{2+} \mid}{\mid F^- \mid}$$

Depending on the value of K and the amount of F^- added, $\mid Fe^{3+} \mid$ varies. The more stable the complex, and also the more F^- is added, the smaller is $\mid Fe^{3+} \mid$, the ion Fe^{3+} is more and more sequestered into the complex FeF^{2+}, and becomes more and more difficult to detect. This property is frequently utilized in analysis in order to mask a given ion.

Applications.—(1) *Detection of Fe^{3+} by thiocyanate.*—If to a solution of ferric iron of about $M/100$ concentration an equal amount of $M/100$ thiocyanate be added, the rather unstable but very intense red-coloured complex $FeCNS^{2+}$ is formed :

$$Fe^{3+} + CNS^- \rightleftharpoons FeCNS^{2+}; \quad pK = 2 \cdot 9$$

The intensity of the red coloration is a measure of the concentration of the complex. If we continue to add dilute CNS^-, then CNS^- saturated, the concentration of $FeCNS^{2+}$ increases. As a result, the use of CNS^- to detect Fe^{3+} is most sensitive, when the concentration of CNS^- is largest, hence: to one drop of the solution add a drop of saturated NH_4CNS.

(2) *Detection of Fe^{2+} by o-phenanthroline.*—o-Phenanthroline gives with Fe^{2+} a very stable red complex:

$$3o\text{-ph.} + Fe^{2+} \rightleftharpoons o\text{-ph}_3.Fe^{2+}; \quad pK = 17 \cdot 7$$
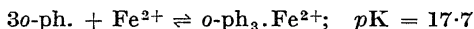
and the equilibrium is displaced towards the right. When exactly 3 molecules of o-phenanthroline are added to $1Fe^{2+}$, practically all the ferrous Fe in the solution goes into the complex state. Excess of reagent has thus no influence on the coloration obtained.

(3) *Differences in stability of ferric complexes.*—If a number of identical solutions of ferric perchlorate or nitrate are prepared (Fe^{3+} is practically colourless) and different complex-forming substances are added to these solutions in equivalent concentrations, then solutions of different colours are formed

Yellow: Cl^-: $FeCl^{2+} \rightleftharpoons Fe^{3+} + Cl^-$ . . . . . . $pK = 1 \cdot 4$
Colourless: H_3PO_4: $FeHPO_4^+ \rightleftharpoons Fe^{3+} + HPO_4^{2-}$ . . $pK = 9 \cdot 4$
Yellow: $H_2C_2O_4$: $Fe(C_2O_4)_3^{3-} \rightleftharpoons Fe^{3+} + 3C_2O_4^{2-}$ . . . $pK = 19 \cdot 2$
Orange: CN^-: $Fe(CN)_6^{3-}$ . . . . pK very large

Add CNS^- to reveal the concentration of free Fe^{3+} in the solution. The intensity of red shows that Fe^{3+} is increasingly sequestered as we pass from the orthophosphate to the pyrophosphate, and then to the oxalate complex. In solutions of the perfect complex $Fe(CN)_6^{3-}$ it is impossible to detect Fe^{4+} by any known reagent.

POLYCOMPLEXES, AMPHOLYTES, DISPROPORTIONA-TION.

—Polycomplexes can donate several particles in succession. Thus $Hg(CNS)_4{}^{2-}$:

$$Hg(CNS)_4{}^{2-} \rightleftharpoons Hg(CNS)_3{}^- + CNS^- \quad . \quad . \quad . \quad pk_4 = 0.6$$
$$Hg(CNS)_3{}^- \rightleftharpoons Hg(CNS)_2 + CNS^- \quad . \quad . \quad . \quad pk_3 = 1.7$$
$$Hg(CNS)_2 \rightleftharpoons HgCNS^+ + CNS^- \quad . \quad . \quad . \quad \left. \begin{matrix} pk_2 \\ pk_1 \end{matrix} \right\} = 19.7$$
$$HgCNS^+ \rightleftharpoons Hg^{2+} + CNS^- \quad . \quad . \quad . \quad .$$
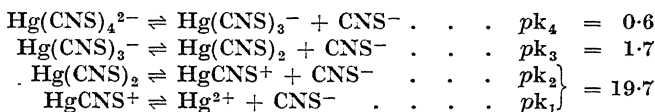
It appears that we should always have $pk_4 < pk_3 < pk_2 < pk_1$, which is the same as saying that CNS^- is more and more strongly sequestered in going from the top to the bottom of the table. Inversely, Hg^{2+} is less and less strongly sequestered.

We thus define the overall constant K_{1-4} for the overall process

$$Hg(CNS)_4{}^{2-} \rightleftharpoons Hg^{2+} + 4CNS^-$$
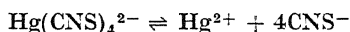
as

$$K_{1-4} = \frac{|\,Hg^{2+}\,|.|\,CNS^-\,|^4}{|\,Hg(CNS)_4{}^{2-}\,|}$$

whence $pK_{1-4} = pk_1 + pk_2 + pk_3 + pk_4 = 22$.

The compound $HgCNS^+$ is the donor in the equilibrium (I) (pk_1) and the acceptor in equilibrium (II) (pk_2): it is an ampholyte and we have the disproportionation equilibrium $2HgCNS^+ \rightleftharpoons Hg(CNS)_2 + Hg^{2+}$.

The characteristic concentration for the solution of an ampholyte is given by the usual formula. Here for $HgCNS^+$ we have

$$pCNS^- = \tfrac{1}{2}(pk_1 + pk_2)$$

Polynuclear complexes.—The most frequent type of complex is that in which the anions or molecules are grouped around a cation: $Fe(CN)_6{}^{4-}$, $Cu(NH_3)_m{}^{2+}$. But other types are known such as $Cd_2(C_2O_4)^{2-}$, $Ag_2I_6{}^{4-}$. Associations of molecules or atoms and of anions can occur: $S_m{}^{2-}$, I_2Cl^-, etc.

Compounds with the ions of water, $Cr_2O_7{}^{2-}$ for example, are referred to as 'condensed' ions.

When the structure involves several central atoms, the complexes are said to be 'polynuclear'.

Dilution of complexes.—We have already seen (p. 32) that a degree of dissociation α can be defined, and that the stability constant is related to α by the relation $K_c = \dfrac{\alpha^2.c}{1-\alpha}$, where c is the total concentration of the complex.

K/c	% Dissociation	K/c	% Dissociation
$\leqslant 10^{-6}$.	$\leqslant 0.1$ complex stable	10 . .	90
10^{-4} .	1	10^2 .	99
10^{-2} .	10	$\geqslant 10^3$.	$\geqslant 99.9$ complex unstable
0.5 . .	50		

For a given value of K, decrease of c (dilution) causes the complex to dissociate. If there are several successive complexes, they can be destroyed one after the other.

Example.—As we have seen, when mercury thiocyanate is dissolved, the following equilibria are set up:

$Hg(CNS)_4{}^{2-} \rightleftharpoons Hg(CNS)_3{}^- + CNS^-$ . . . . $pk_4 = 0.6$

$Hg(CNS)_3{}^- \rightleftharpoons Hg(CNS)_2 + CNS^-$ . . . . $pk_3 = 1.7; pk_2 = 10$
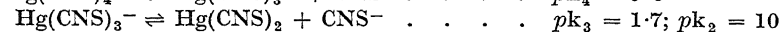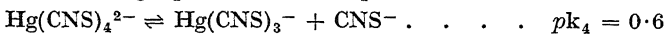
whence the following table:

c	k_4/c	$\alpha_4 \times 100$	k_3/c	$\alpha_3 \times 100$	k_2/c	$\alpha_2 \times 100$
10^{-1}	$10^{0.4}$	75	$10^{-0.7}$	35	10^{-9}	0
10^{-2}	$10^{2.4}$	99.6	$10^{1.3}$	95	10^{-7}	0
10^{-3}	$10^{4.4}$	100	$10^{3.3}$	99.9	10^{-5}	0.002

It is seen that dilution causes $Hg(CNS)_4{}^{2-}$, then $Hg(CNS)_3{}^-$ to disappear. $Hg(CNS)_2$ is much more stable, and resists decomposition.

Experiments.—(1) *Destruction of complexes by dilution.*—Prepare a solution of the ferric thiocyanate complex.

$$FeCNS^{2+} \rightleftharpoons Fe^{3+} + CNS^- \quad . \quad . \quad . \quad pK = 2.9$$

Divide the solution into two equal parts and dilute one of them. By observing the colour of the solution by looking down the tube, the total quantity of $FeCNS^{2+}$ in solution can be assessed. Comparing thus the colours in the two tubes, it will be seen that dilution has caused part of the complex to disappear.

The same test can be carried out on the more stable ferrous *o*-phenanthroline complex:

$$o\text{-ph.}_3Fe^{2+} \rightleftharpoons 3o\text{-ph.} + Fe^{2+}; \quad pK = 17.7$$
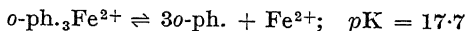
Dilution has no visible influence on this more stable complex.

(2) *Dilution of cobaltothiocyanate complexes.*—To a pale-rose solution of a cobalt salt Co^{2+} add, a little at a time, a concentrated solution of CNS^-. A series of complexes are formed in succession: $CoCNS^+$, $Co(CNS)_2$, etc. The first are a more intense red than Co^{2+}, the later ones are blue.

When the higher blue complexes are obtained, for instance $Co(CNS)_4{}^{2-}$, dilute the solution slowly. The higher complexes are destroyed first and the blue colour disappears.

INFLUENCE OF THE IONIC STRENGTH OF THE SOLUTION.—Consider a complex, for example $FeCNS^{2+}$. We have

$$\frac{|Fe^{3+}| \cdot |CNS^-|}{|FeCNS^{2+}|} = K$$

whence

$$\frac{C_{Fe^{3+}} \cdot f_{Fe^{3+}} \times C_{CNS^-} \cdot f_{CNS^-}}{C_{FeCNS^{2+}} \cdot f_{FeCNS^{2+}}} = K$$

or

$$\frac{C_{Fe^{3+}} \cdot C_{CNS^-}}{C_{FeCNS^{2+}}} = K\frac{f_{Fe^{3+}} \cdot f_{CNS^-}}{f_{FeCNS^{2+}}} = K'$$

K' is the apparent equilibrium constant; it has a fixed value for given conditions. If the ionic strength increases, the activity coefficients deviate from unity, and the apparent constant K' increases. The complex behaves as though it were less stable.

Experiment.—To a solution of ferrithiocyanate add some solid sodium nitrate: the colour of the complex disappears gradually.

COMPLEXES AND ACIDITY
(EXCHANGE OF PROTONS AND IONS)

INFLUENCE OF pH ON THE EQUILIBRIUM OF COMPLEXES

COMPLEXES CONTAINING A BASE.—Consider the ferrifluoride complex, FeF^{2+}. In water the following equilibria are set up:

$$FeF^{2+} \rightleftharpoons Fe^{3+} + F^- \quad \text{with} \quad \frac{|Fe^{3+}| \cdot |F^-|}{|FeF^{2+}|} = K_c \quad \bullet \quad \text{(I)}$$
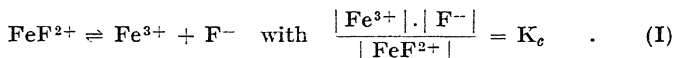
F^- is a base, and consequently:

$$F^- + H^+ \rightleftharpoons HF \quad \text{with} \quad \frac{|F^-| \cdot |H^+|}{|HF|} = K_A \quad \bullet \quad \bullet \quad \text{(II)}$$
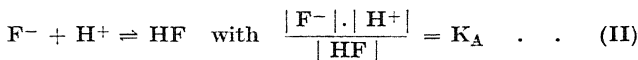
If an acid is added to a solution of the FeF^{2+} complex the F^- ions will disappear, and the equilibrium (II) will be displaced towards the right, which causes the equilibrium (I) also to be displaced towards the right; the complex ions dissociate, and Fe^{3+} ions appear.

An approximate calculation enables us to describe the phenomena more precisely. Suppose we introduce the complex FeF^{2+} at the total concentration c, we shall then have, supposing the complex to be sufficiently stable, $|FeF^{2+}| \simeq c$.

On the other hand, the total concentration of fluorine is equal to that of iron:

$$|FeF^{2+}| + |F^-| + |HF| = |FeF^{2+}| + |Fe^{3+}|$$

whence $\quad\quad\quad |F^-| + |HF| = |Fe^{3+}|$

Besides this, there are the relations in (I) and (II) involving the constants K_c and K_A, whence

$$|Fe^{3+}| = \sqrt{K_c \cdot c \left(1 + \frac{|H^+|}{K_A}\right)}$$

This formula, which gives the value of Fe^{3+} as a function of pH, is valid only in the region where the complex is sufficiently stable.

It will be noted that $|Fe^{3+}|$ depends on the initial concentration as well as on the pH, and on the stability constant of the complex and on that of the acid-base pair involved. More of the complex is destroyed the more acid the solution, the stronger the base, and the less stable the complex is initially.

Influence of pH and of pK$_A$.—When $|H^+| < K_A$ or pH $> p$K$_A$, $|H^+|/K_A$ rapidly becomes negligible relative to unity, and

$$|Fe^{3+}| = \sqrt{K_c \cdot C}$$

pH has thus no influence.

When pH $< p$K$_A$, $|H^+|/K_A$ rapidly becomes extremely large relative

to unity, and then $| Fe^{3+} | = \sqrt{K_c c . | H^+ |}/K_A$. Thus $| Fe^{3+} |$ is proportional to $| H^+ |^{\frac{1}{2}}$. These results are depicted in fig. 7. Here $K_A = 10^{-3.2}$. Above pH 3·2 the stability of the complex does not change. Below pH 3·2 the complex gradually liberates Fe^{3+} ions; but, since K_c comes in as a factor, the concentration of ferric ions is not appreciable above this pH. With very stable complexes the pH can be very much lower than pK_A. A pH can be defined, below which the complex can be considered as stable.
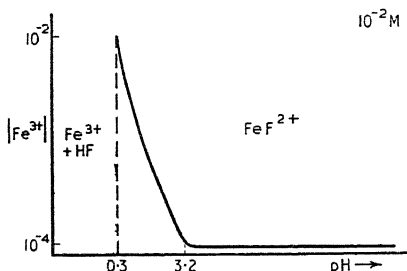
FIG. 7.—APPARENT STABILITY OF FeF^{2+} COMPLEX AS A FUNCTION OF pH

With the carbonate complexes, $pk_1 = 10.2$, hydrosulphide complexes, $pk_1 = 14.9$, phosphate, $pk_1 = 12.3$, etc., the destruction of the complex commences even in alkaline solution.

With the very stable $Fe(CN)_6^{4-}$, $Ag(CN)_2^{-}$, $Co(NH_3)_6^{3+}$, the destruction of the complex is inappreciable even at a pH of 0.

Another example.—In a solution of mercury cyanide, $Hg(CN)_2$, M/10, the concentration of Hg^{2+} ions varies with pH according to the relations

$$\frac{| Hg^{2+} | . | CN^- |^2}{| Hg(CN)_2 |} = 10^{-21} \quad \text{and} \quad \frac{| CN^- | . | H^+ |}{| HCN |} = 10^{-9.1}$$

In the region where the complex is stable, that is to say where $| Hg^{2+} |$ is negligible compared with $| Hg(CN)_2 |$, we find, proceeding as before,

$$| Hg^{2+} | = \sqrt[3]{10^{-22.6}\left(1 + \frac{| H^+ |}{10^{-9.1}}\right)^2}$$

Right up to a pH of 9·1, the concentration of Hg ions is independent of pH. At pH 5, the concentration of Hg ions is still only 10^{-5}, i.e. negligible. Even at pH of 1, approximately 90 per cent of the $Hg(CN)_2$ remains undissociated.

Influence of an excess of reagent.—Returning to the example of FeF^{2+}, the addition of excess F^- causes a decrease in the activity of the free Fe^{3+} and as a result the destruction of the complex is shifted to more acid regions.

Ammonia complexes (ammines).—These complexes are numerous. Ammonia is a base, and as a result these complexes are less stable in acid solution because NH_4^+ ions are formed:

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
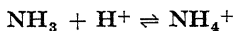
The addition of ammoniacal salts containing NH_4^+ to the solution, on the other hand, displaces the equilibrium to the left and increases the stability.

The cobaltiammines, which are very stable complexes, are not always destroyed in acid solution. On the other hand, complexes with Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} are destroyed.

Hydrosulphide complexes.—In the presence of an excess of S^{2-} ions, that is to say when sulphide is present in excess, certain sulphides, of arsenic, tin, antimony, etc., dissolve as hydrosulphide complexes. There is a certain analogy between this and the dissolution of hydroxides in alkalis. The O^{2-} ions are replaced here by the S^{2-} ions, which are strong bases (pK 15). These complexes are destroyed in acid solution.

Complexes with neutral ions.—CNS^-, Cl^-, NO_3^- are very weak bases not capable of accepting protons. The corresponding complexes are not influenced by pH changes.

Complexes involving an acid.—The same remarks apply here. These complexes are less stable in alkaline solution.

Thus in

$$BF_4^- \rightleftharpoons B^{3+} + 4F^-$$
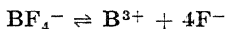
B^{3+} is a very strong acid:

$$B^{3+}, 3H_2O \rightleftharpoons B(OH)_3 + 3H^+$$
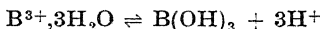
BF_4^- is not stable in alkaline solution.

Experiments and applications

(1) *Influence of pH on the cupriammine complexes.*—Add to a dilute solution of a copper salt a little ammonia NH_3. If the solution is acid, the H^+ ions disappear to give NH_4^+ ions, and a buffer mixture NH_4^+—NH_3 finally results, having a pH of approximately 9. The intense blue cupriammine complexes, $Cu(NH_3)^{2+}{}_m$, are then stable. Inversely, addition of acid destroys the complexes and the blue coloration disappears when the pH has fallen sufficiently low.

(2) *Detection of cobalt Co^{2+} in the presence of Fe^{3+}.*—Make the following tests: (*a*) To an acid solution of Fe^{3+} add CNS^-: the red complex $FeCNS^{2+}$ is formed. CNS^- is an extremely weak base (HCNS is a 'strong' acid) so that variations of pH are without influence on CNS^-. Add fluoride F^- to the solution: this is a base, the H^+ ions are used up to produce HF and finally the buffer mixture F^-/HF is arrived at. At this pH the fluoride complex FeF^{2+} becomes stable, more stable than $FeCNS^{2+}$, and the red coloration due to $FeCNS^{2+}$ disappears. If now a strong acid is added, the pH decreases, the complex FeF^{2+} will be more or less destroyed, and the red coloration of $FeCNS^{2+}$ partially reappears.

(*b*) Co^{2+} gives with CNS^- complexes of low stability, such as $Co(CNS)_4^{2-}$, which are blue. A large excess concentration of CNS^- is necessary to get this coloration. The addition of F^- has no effect.

(*c*) Fe^{2+} and Co^{2+} can thus be detected as follows. A drop of the solution to be examined is taken, and a drop of saturated NH_4CNS solution added; the red coloration of $FeCNS^{2+}$ indicates the presence of Fe^{3+}. This very strong colour masks the blue colour of cobalt. Add solid sodium fluoride gradually until the red colour of $FeCNS^{2+}$ disappears. The blue coloration of Co^{2+} is then visible (we shall see that this colour can be made more perceptible by the addition of alcohol).

DISPLACEMENT OF ACID-BASE EQUILIBRIA BY THE FORMATION OF COMPLEXES

Example.—Consider hydrocyanic acid HCN:

$$HCN \rightleftharpoons CN^- + H^+; \quad pK_A = 9 \cdot 1 \quad . \quad . \quad . \quad (I)$$

If Ag ions are added in small quantity, then

$$2CN^- + Ag^+ \rightleftharpoons Ag(CN)_2^-; \quad pK_c = 20 \cdot 9$$
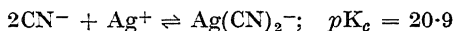
The CN^- ions disappear, and the hydrocyanic acid ionizes because of the displacement of equilibrium (I) to the right. The solution becomes more acid. It can therefore be said that the disappearance of one of the acid or basic ions by the formation of a complex ion apparently reinforces the properties of the conjugate acid or base.

Note.—This is not valid unless the base formed, here $Ag(CN)_2^-$, is so weak $(HAg(CN)_2$ is a sufficiently strong acid) that the H^+ ions remain free. This is certainly the case whenever a stable complex is formed.

Experiments.—(1) Take a solution of ammonium sulphate. It is acid and if a drop of methyl red is added an orange colour is obtained—pH 5 approximately. If to this solution Ag^+ ions are added via a solution of $AgNO_3$, then the NH_3 disappears as a result of the formation of argento-ammine complexes.

$$NH_3 + Ag^+ \rightleftharpoons AgNH_3^+$$
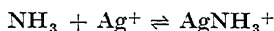
The solution becomes more acid, and the methyl red turns red.

(2) A solution of cyanide CN^- is basic $(pK = 9 \cdot 2)$ and the addition of a drop of bromothymol blue turns the solution blue $(pH \geqslant 7 \cdot 6)$. Add a drop of dilute acid: the solution remains alkaline.

On the other hand, if a solution of mercuric chloride is previously neutralized using the same indicator, and the two solutions are mixed adding an excess of the mercuric chloride solution to that of the cyanide, CN^- disappears.

$$Hg^{2+} + CN^- \rightleftharpoons HgCN^+$$
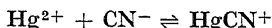
The solution ceases to be alkaline, and the indicator turns yellow, $pH < 6 \cdot 0$.

COMPLEXES WITH THE IONS OF WATER

Water and its ions play a special role in aqueous solution. Water can donate H^+, H_2O, OH^-, O^{2-}.

Complexes with H^+ are acids.

All ions are complexes with water molecules (solvation). They have special properties because of the constant and very large concentration of H_2O. We shall study them in the second part of this volume.

Complexes with OH^-, O^{2-} are very numerous. Because of the acid and basic properties of the different particles, the corresponding complexes are influenced by pH.

Mono acid cations.—The hydrated cation M^+,H_2O is a polyacid:

$$M^+,H_2O \rightleftharpoons MOH + H^+ \quad . \quad . \quad . \quad . \quad (I)$$
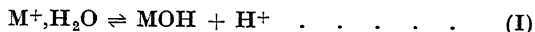
with

$$\frac{|MOH| \cdot |H^+|}{|M^+|} = k_2$$

$$\text{MOH} \rightleftharpoons \text{MO}^- + \text{H}^+ \quad . \quad . \quad . \quad . \quad . \quad \text{(II)}$$

with

$$\frac{|\,\text{MO}^-\,|\,.\,|\,\text{H}^+\,|}{|\,\text{MOH}\,|} = k_1$$

In acid solution, the two equilibria are displaced towards the left. Going from alkaline to acid solutions, the anion, then the hydroxide, and finally the cation are encountered.

According to (I) we have

$$\frac{|\,\text{M}^+\,|}{|\,\text{MOH}\,|} = \frac{|\,\text{H}^+\,|}{k_2}$$

Since $|\,\text{H}^+\,| > k_2$ or $p\text{H} < pk_2$, $|\,\text{M}^+\,|$ becomes larger than $|\,\text{MOH}\,|$. Thus the cation predominates. From (II), it is seen that the anion predominates when $p\text{H} > pk_1$.

If the cation is very acid, pk_2 is smaller than $-1 \cdot 7$, and the cation ceases to exist in aqueous solution. Similarly, if pk_1 is greater than $15 \cdot 7$, the very basic anion ceases to exist in aqueous solution.

M$^+$	MOH	MO$^-$

$$p\text{H} \qquad pk_2 \qquad\qquad pk_1$$
$$\text{H}_3\text{O}^+ \qquad\qquad\qquad\qquad \text{OH}^-$$
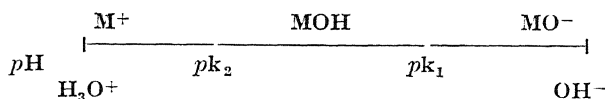
Formulae of hydroxides.—In the same way as the formulae of ions have been simplified by omitting the water of hydration, those of hydroxides will be simplified by omitting from their formulae all water molecules not necessary for the explanation of their properties.

Thus the simplest ferric hydroxide has the formula FeO_2H. In Fe(OH)_3 the strongest acidity is already very weak, and the others can be neglected.

Polyacid cations.—When a cation carries several charges, there are several acid-base pairs thus:

$$\text{Al}^{3+}, \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+$$

$$\text{AlOH}^{2+} \rightleftharpoons \text{AlO}^+ + \text{H}^+, \text{ etc.}$$
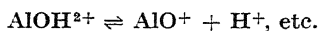
Examples are cations such as UO_2^{2+}, VOOH^+, Ce(OH)^{3+}, etc.

Examples.—Ions derived from boron. We have

$$\text{B}^{3+}, 3\text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_3 + 3\text{H}^+$$

$$\text{B(OH)}_3 \rightleftharpoons \text{H}_2\text{BO}_3^- \text{ (or BO}_2^-) + \text{H}^+$$
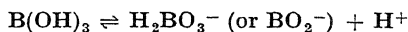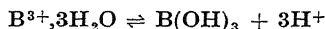
B^{3+} is very acid and does not exist in water (or if it does, its concentration is quite negligible). When BCl_3 is introduced into water, even in very acid solution, boric acid B(OH)_3 (or BO_2H) is obtained.

In alkaline solution, BO_2^- is formed.

B^{3+}	HBO$_2$	BO$_2^-$

$$p\text{H} \qquad -1 \cdot 7 \qquad\qquad 9 \qquad\qquad 15 \cdot 7$$
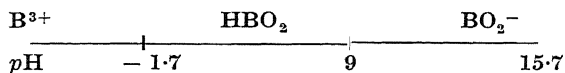
Ions derived from P^{5+}.—With phosphorus in the fifth state of oxidation, P(V), we have

P^{5+}...	H$_3$PO$_4$	H$_2$PO$_4^-$	HPO$_4^{2-}$	PO$_4^{3-}$

$$p\text{H} \qquad -1 \cdot 7 \quad 2 \cdot 2 \qquad\quad 7 \cdot 2 \qquad\quad 12 \cdot 3 \quad 15 \cdot 7$$

5
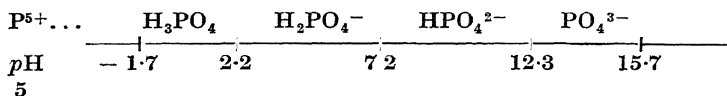
Monobasic anions.—With the simple anion A^-, we get in a similar way:

$$A^- + H^+ \rightleftharpoons HA \quad \text{with} \quad \frac{|\,A^-\,|\cdot|\,H^+\,|}{HA} = k_1$$

$$HA + H^+ \rightleftharpoons H_2A^+ \quad \text{with} \quad \frac{|\,HA\,|\cdot|\,H^+\,|}{|\,H_2A^+\,|} = k_2$$

H_2A^+		HA		A^-
pH	pk$_2$		pk$_1$	
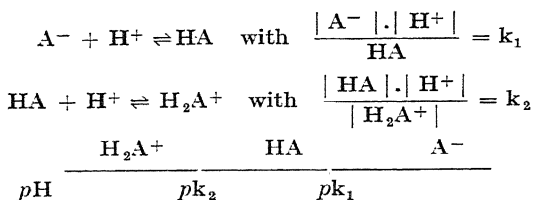
Examples.—(*a*) *Ions derived from oxygen.*—

H_3O^+		H_2O		OH^-	O^{2-}
pH	$-1\cdot7$		$15\cdot7$		
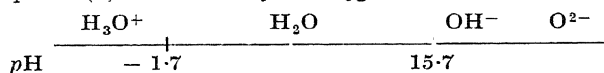
Between the limits of pH $-1\cdot7$ and $15\cdot7$ molecules of water alone exist.

(*b*) *Ions derived from nitrogen.*—N^{3-}, NH^{2-}, NH_2^-, being very basic, do not exist in aqueous solution.

NH_4^+		NH_3
pH	$-1\cdot7$	$9\cdot2$
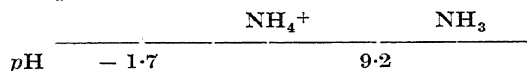
(*c*) *Ions derived from iodine.*—The sole ion existing over the whole pH range is I^-.

COMPLEXES AND OXIDATION-REDUCTION (EXCHANGE OF IONS AND ELECTRONS)

I. Changes in oxidation-reduction properties as a result of the formation of complexes

CONSIDER the oxidation-reduction system:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \quad \text{with} \quad E = E_0 + 0.06 \log \frac{|Fe^{3+}|}{|Fe^{2+}|} \qquad \text{(I)}$$
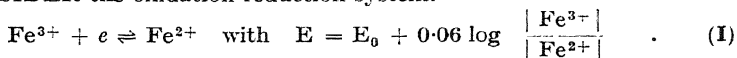
The addition of fluoride ions to the solution causes the complex ion FeF^{2+} to be formed.

$$Fe^{3+} + F^- \rightleftharpoons FeF^{2+} \quad \text{with} \quad \frac{|Fe^{3+}| \cdot |F^-|}{|FeF^{2+}|} = K \quad \text{(II)}$$
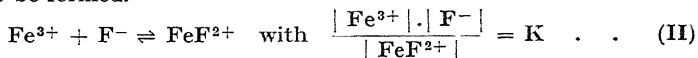
The addition of fluoride ions causes ferric ions to disappear, the ratio $|Fe^{3+}Fe|/|^{2+}|$ decreases, E is reduced, the solution becomes less oxidizing and thus more reducing.

Thus in the presence of fluoride ions ferric ions are weaker oxidants, whilst ferrous ions are stronger reductants.

The formation of a complex apparently weakens the oxidizing or reducing power of the complexed ion. The properties of the conjugate ion are apparently reinforced.

Potential of a complex system

Here, equilibrium (III) corresponds to equilibria (I) and (II).

$$FeF^{2+} + e \rightleftharpoons Fe^{2+} + F^- \quad \text{. . . . . . (III)}$$
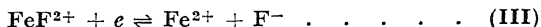
and we have

$$E = E_0 + 0.06 \log \frac{|Fe^{3+}|}{|Fe^{2+}|} = E_0 + 0.06 \log \frac{K_c |FeF^{2+}|}{|Fe^{2+}| \cdot |F^-|}$$

$$= E_0 + 0.06 \log K_c + 0.06 \log \frac{|FeF^{2+}|}{|Fe^{2+}| \cdot |F^-|}$$

Thus a new normal potential can be defined: $E'_0 = E_0 + 0.06 \log K_c$ for system (III).

E will thus be smaller, the smaller K_c, the more stable the complex, and also the larger the concentration $|F^-|$ of the complex-forming ion.

Case where both oxidant and reductant are 'complexed'.— Consider the oxidation-reduction system:

$$Co^{3+} + e \rightleftharpoons Co^{2+} \quad \text{with} \quad E = 1.84 + 0.06 \log \frac{|Co^{3+}|}{|Co^{2+}|} \text{ volts}$$
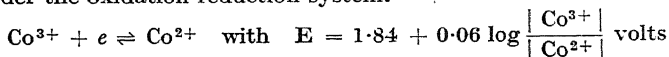
If CN^- ions are added in sufficient quantity the Co^{3+} and Co^{2+} ions will disappear with formation of the cyanide complexes, $Co(CN)_6^{3-}$ and, possibly, of $Co(CN)_6^{4-}$. We have the relationships:

$$Co(CN)_6^{3-} \rightleftharpoons Co^{3+} + 6CN^- \quad \text{with} \quad \frac{|Co^{3+}| \cdot |CN^-|^6}{|Co(CN)_6^{3-}|} = K_{Ox}$$

and

$$Co(CN)_6^{4-} \rightleftharpoons Co^{2+} + 6CN^- \text{ with } \frac{|\ Co^{2+}\ |.|\ CN^-\ |^6}{|\ Co(CN)_6^{4-}\ |} = K_{Red}$$
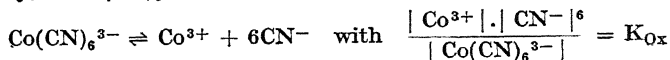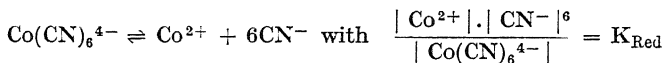
whence

$$E = 1{\cdot}84 + 0{\cdot}06 \log \frac{K_{Ox}}{K_{Red}} \frac{|\ Co(CN)_6^{3-}\ |}{|\ Co(CN)_6^{4-}\ |}$$

$$= 1{\cdot}84 + 0{\cdot}06 \log \frac{K_{Ox}}{K_{Red}} + 0{\cdot}06 \log \frac{|\ Co(CN)_6^{3-}\ |}{|\ Co(CN)_6^{4-}\ |} \text{ volts}$$

To the new oxidation-reduction system:

$$Co(CN)_6^{3-} + e \rightleftharpoons Co(CN)_6^{4-}$$
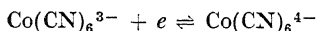
corresponds the normal potential

$$E'_0 = 1{\cdot}84 + 0{\cdot}06 \log \frac{K_{Ox}}{K_{Red}} \text{ volts}$$

Experiment gives $E'_0 = -0{\cdot}83$ volt.

The system has thus become strongly reducing, since $K(Ox)/K(Red) = 10^{-44}$: the cobalticyanide complex is vastly more stable than the cobaltocyanide one. The ratio $\dfrac{|\ Co^{3+}\ |}{|\ Co^{2+}\ |}$ has become very small.

Note.—These deductions are applicable in cases where the equilibria are set up between the simple and complex ions, and when they set up quickly enough. This is undoubtedly not the case for the equilibrium of $Co(CN)_6^{3-}$ with its ions.

Experiments.—(*a*) The reducing power of Co^{2+} in the presence of CN^- ions can be demonstrated thus:

Methylene blue is not reduced by Co^{2+}, nor by CN^-, but when both ions are present together it is decolorized.

To a small amount of a dilute solution of a cobalt salt, add methylene blue solution until a blue tint is obtained. Add a drop of a cyanide solution, also coloured blue with methylene blue; there is instant decolorization.

(*b*) Cu(II) salts have only a small oxidizing power: in particular, they do not oxidize benzidine. In the presence of CN^-, these salts however become strongly oxidizing, because there is a cuprocyanide complex much more stable than the cupricyanide one. Benzidine is then oxidized to a very deep blue.

To a dilute solution of a cupric salt, add a little acetate buffer (*p*H 4·8) then several drops of an alcoholic solution of benzidine. The coloration is still very weak. Add a drop of cyanide; the benzidine is oxidized to an intense blue.

II. Influence of oxidation or reduction on the equilibria of complexes

Reciprocally, complexes can be either stabilized or destroyed by oxidation-reduction.

Experiment.—Form red $FeCNS^{2+}$ by adding CNS^- to Fe^{3+}. Add a drop of stannous chloride: the red colour disappears with the formation of

Fe^{2+} and CNS^-. If Co^{2+} is present, the blue colour of the corresponding complex thiocyanates can be observed.

Normal potentials of certain systems of complexes

$$Co(CN)_6^{3-} + e \rightleftharpoons Co(CN)_6^{4-} \quad . \quad . \quad . \quad . \quad -0.83 \text{ volt}$$

$$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-} \quad . \quad . \quad . \quad . \quad +0.36 \quad ,,$$

$$PtCl_6^{2-} + 2e \rightleftharpoons PtCl_4^{2-} + 2Cl^- \quad . \quad . \quad . \quad 0.76 \quad ,,$$

$$AuCl_4^- + 2e \rightleftharpoons AuCl_2^- + 2Cl^- \quad . \quad . \quad . \quad 0.95 \quad ,,$$

$$PdCl_6^{2-} + 2e \rightleftharpoons PdCl_4^{2-} + 2Cl^- \quad . \quad . \quad . \quad 1.30 \quad ,,$$

Notes.—(*a*) Other values are given in the second part of this volume. When the composition of the complexes is unknown, the values of the formal normal potentials must be used (see p. 19). A certain number of these values are also given in Part II.

(*b*) We shall deal in Chapter VIII with the oxidation-reduction properties of complexes with the ions of water.

ACIDITY AND OXIDATION-REDUCTION
(EXCHANGE OF ELECTRONS AND PROTONS)

I. Changes in oxidation-reduction properties with pH

CONSIDER the oxidant-reductant system quinone-hydroquinone. In sufficiently alkaline solution we have

$$O=C_6H_4=O + 2e \rightleftharpoons {}^-O—C_6H_4—O^-$$
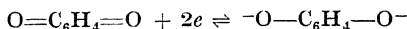
which we will represent, for simplicity, by

$$Q + 2e \rightleftharpoons Q^{2-} \quad \text{with} \quad E = E_0 + 0.03 \log \frac{|\,Q\,|}{|\,Q^{2-}\,|}; \quad E_0 = 0.08 \text{ volt} \quad \text{(I)}$$
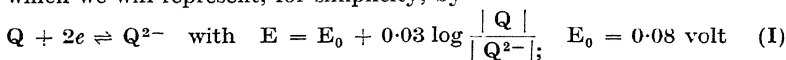
But hydroquinone is dibasic:

$$Q^{2-} + H^+ \rightleftharpoons HQ^- \quad \text{with} \quad \frac{|\,Q^{2-}\,|.|\,H^+\,|}{|\,HQ^-\,|} = k_1 \quad . \quad . \quad \text{(II)}$$

and

$$HQ^- + H \rightleftharpoons H_2Q \quad \text{with} \quad \frac{|\,HQ^-\,|.|\,H^+\,|}{|\,H_2Q\,|} = k_2 \quad . \quad . \quad \text{(III)}$$
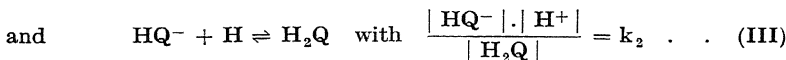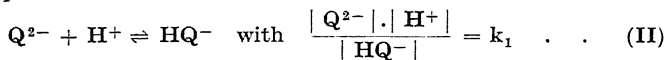
$$pk_2 = 10.0; \quad pk_1 = 11.5$$

Thus if the pH is decreased (solution becomes more acid), Q^{2-} disappears and HQ^- appears; as a result, the ratio Q/Q^{2-} increases, the system becomes apparently more oxidizing.

Note.—We have argued in the same way for complexes (p. 53). Here we are dealing with the disappearance of Q^{2-} by formation of a complex with H^+.

Formal potential.—The problem which confronts the chemist is to predict the potential, at a given pH, of a solution in which are present given total concentrations of quinone and hydroquinone, without going into the details of ionization.

If c and c' are the total concentrations of quinone and hydroquinone respectively, we have

$$|\,Q\,| = c \text{ (omitting activity coefficients)}.$$

$$|\,Q^{2-}\,| + |\,HQ^-\,| + |H_2Q\,| = c'$$

whence, using relations (II) and (III):

$$|\,Q^{2-}\,|\left(1 + \frac{|\,H^+\,|}{k_1} + \frac{|\,H^+\,|^2}{k_1k_2}\right) = c'$$

whence

$$E = E_0 + 0.03 \log \frac{|\,Q\,|}{|\,Q^{2-}\,|} = E_0 + 0.03 \log \frac{c}{c'}\left(1 + \frac{|\,H^+\,|}{k_1} + \frac{|\,H^+\,|^2}{k_1k_2}\right)$$

or

$$E = E_0 + 0.03 \log \left(1 + \frac{|\,H^+\,|}{k_1} + \frac{|\,H^+\,|^2}{k_1k_2}\right) + 0.03 \log \frac{c}{c'}$$

$$= E'_0 + 0.03 \log \frac{c}{c'}$$

In this way, a formal normal potential $(c = c')$ which depends on $p\mathrm{H}$ is defined (fig. 8).

Note.—In reality, an unstable complex 'quinhydrone', a compound between quinone and hydroquinone, is formed.

It will be observed that above $p\mathrm{H} = pk_1 = 11\cdot 5$ practically all the hydroquinone is in the form of Q^{2-}. Thus the system $\mathrm{Q}^{2-} - 2e \rightleftharpoons \mathrm{Q}$ exists. In the general formula for the potential, $|\mathrm{H}^+|/k_1$ and $|\mathrm{H}^+|^2/k_1k_2$ are negligible compared with unity and $\mathrm{E} = \mathrm{E}_0 + 0\cdot 03 \log c/c'$ with $\mathrm{E}_0 = 0\cdot 08$ volt.

For $pk_2 < p\mathrm{H} < pk_1$, the predominant form is HQ^-. The oxidation-reduction system is then

$$\mathrm{HQ}^- - 2e \rightleftharpoons \mathrm{Q} + \mathrm{H}^+$$
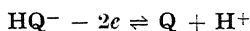
with $\quad \mathrm{E} = \mathrm{E}_1 + 0\cdot 03 \log \dfrac{|\,\mathrm{Q}\,|\cdot|\,\mathrm{H}^+\,|}{|\,\mathrm{HQ}^-\,|} = \mathrm{E}_1 + 0\cdot 03 \log \mathrm{H}^+ + 0\cdot 03 \log \dfrac{c}{c'}$

$$= \mathrm{E}_1 + 0\cdot 03 \log p\mathrm{H} + 0\cdot 03 \log \frac{c}{c'}$$

This corresponds to the fact that in the general formula, $|\,\mathrm{H}^+\,|/k_1$ is then very large relative both to unity and $|\,\mathrm{H}^+\,|^2/k_1k_2$. We can deduce that $\mathrm{E}_1 = \mathrm{E}_0 - 0\cdot 03 \log k_1 = 0\cdot 41$ volt.

Finally, for $p\mathrm{H} < pk_2$, all the hydroquinone is in the form of $\mathrm{H}_2\mathrm{Q}$, and we are then dealing with the oxidation-reduction system

$$\mathrm{H}_2\mathrm{Q} - 2e \rightleftharpoons \mathrm{Q} + 2\mathrm{H}^+$$
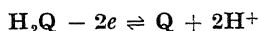
with $\quad \mathrm{E} = \mathrm{E}_2 + 0\cdot 03 \log \dfrac{|\,\mathrm{Q}\,|\cdot|\,\mathrm{H}^+\,|^2}{|\,\mathrm{H}_2\mathrm{Q}\,|} = \mathrm{E}_2 - 0\cdot 06\, p\mathrm{H} + 0\cdot 03 \log \dfrac{c}{c'}$

which corresponds to neglecting, in the general formula, unity and $|\,\mathrm{H}^+\,|/k_1$ relative to $|\,\mathrm{H}^+\,|^2/k_1k_2$. We find:

$$\mathrm{E}_2 = \mathrm{E}_0 - 0\cdot 03 \log k_1 - 0\cdot 03 \log k_2 = 0\cdot 70 \text{ volt}$$

We have thus defined two new normal potentials, E_1 and E_2.

Oxidation-reduction properties of complexes with the ions of water as a function of pH

For the system ($V(V)/V(IV)$), the usual normal potential is given by

$$V^{5+} + e \rightleftharpoons V^{4+} \quad \text{with} \quad E = E_5 + 0.06 \log \frac{|\ V^{5+}\ |}{|\ V^{4+}\ |}$$
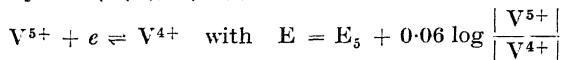
but V^{5+},aq. is a strong acid and, even in acid solution, the cation VO_2^+,aq. is formed:

$$V^{5+}, 2H_2O \rightleftharpoons VO_2^+ + 4H^+$$
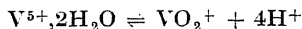
similarly V^{4+} is too acid to exist in water:

$$V^{4+}, H_2O \rightleftharpoons VO^{2+} + 2H^+$$

We have in practice a new oxidation-reduction system

$$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O$$
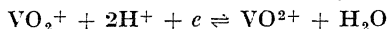
for which a new potential can be defined as before. This potential is related to E_5 by the acidity constants of the V^{5+}/VO_2^+ and V^{4+}/VO^{2+} pairs:

$$E = E'_5 + 0.06 \log \frac{|\ VO_2^+\ |\ .\ |\ H^+\ |^2}{|\ VO^{2+}\ |}$$

which can be expressed as:

$$E = E'_5 - 0.12\,pH + 0.06 \log \frac{|\ VO_2^+\ |}{|\ VO^{2+}\ |} = E''_5 + 0.06 \log \frac{|\ VO_2^+\ |}{|\ VO^{2+}\ |}$$

E'_5 is known to the chemist, as also is $|\ VO_2^+\ |$ and $|\ VO^{2+}\ |$. It is convenient to represent E''_5 as a function of pH (fig. 9).

Other examples.—The following oxidation-reduction systems involve electrons and protons:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$$
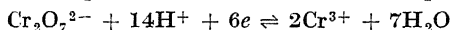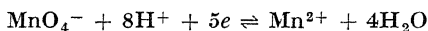
If equivalent quantities of oxidant and reductant are mixed, the formal potential varies with pH. The corresponding curves are given in Part II for a large number of systems.

Fields of predominance of ions and molecules as a function of pH and of oxidation-reduction potential

Turning our attention to the curve in fig. 8: for $pH = pk_2$ (line BE), we have $|\ H_2Q\ | = |\ HQ^-\ |$; for $pH = pk_1$ (line CF), we have $|\ HQ^-\ | = |\ Q^{2-}\ |$. To the left of BE, H_2Q predominates; to the right of CF, Q^{2-}; between the two lines, HQ^-. The curve ABCD indicates the potential for $|\ \text{total Quinone}\ | = |\ \text{total Hydroquinone}\ |$; for AB, $|\ Q\ | = |\ H_2Q\ |$, for BC, $|\ Q\ | = |\ HQ^-\ |$, and for CD, $|\ Q\ | = |\ Q^{2-}\ |$, more or less exactly. Above this curve, the potential is higher and quinone predominates; below it, the various forms of hydroquinone depending on the pH. In this way the fields of potential and of pH in which each form predominates are delineated.

Note.—The different lines in reality flow smoothly into one another without sharp 'corners'.

Use of the curves of formal oxidation-reduction potential against pH.—Take for example the curves relating to the systems $V(V)/V(IV)$ and $I°/I^-$. It can be seen from these curves (fig. 9) that the

vanadates oxidize the iodides in acid solution, whereas in neutral or alkaline solution iodine oxidizes vanadyl salts.

From a knowledge of the curves for different systems the oxidation-reduction reactions in all solutions can be predicted.

Note.—The reactions can be slow (see p. 108), and the predictions are not verified.

Experiments.—(a) The curve representing As(V)/As(III) is analogous to that for the V(V)/V(IV) system. Arsenic acid, As(V), oxidizes iodides in acid solution, and iodine oxidizes arsenious acid, As(III), in neutral solution.
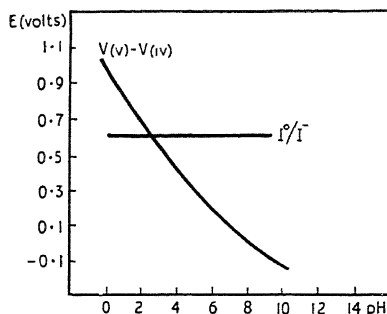
FIG. 9.—FORMAL NORMAL POTENTIALS FOR THE SYSTEM V(V)/V(IV) AND $I_2/2I^-$ AS A FUNCTION OF pH

To a solution containing arsenious and arsenic acids adjusted to a pH of 8 by addition of sodium bicarbonate, add a little iodine and starch solution. The iodine is reduced and the solution remains colourless. Acidify the solution strongly; the iodide is oxidized, iodine is formed and the starch becomes coloured an intense blue.

(b) The ferricyanide-ferrocyanide system:
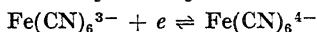
$$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$$

has a potential independent of pH above pH 4. Below this, the formal normal potential rises (fig. 10) apparently by disappearance of $Fe(CN)_6^{4-}$ to form $HFe(CN)_6^{3-}$.
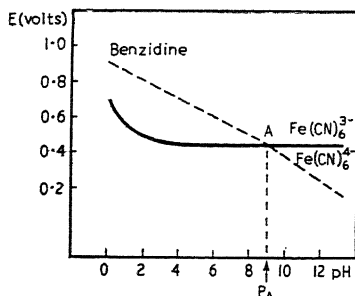
FIG. 10.—FORMAL NORMAL POTENTIAL OF THE SYSTEMS $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ AND OF BENZIDINE/OXIDIZED BENZIDINE AS A FUNCTION OF pH

Colourless benzidine can be oxidized to a blue form and the formal potential for the system is reproduced in fig. 10. The two curves cross at A.

Make a mixture of solutions of ferrocyanide-ferricyanide, which is a buffer fixing the oxidation potential at $E = 0.45$ volt.

Add a drop of benzidine in alcoholic solution. In a solution where $pH < p_A$, the benzidine remains in the colourless form; at $pH > p_A$, the benzidine is oxidized and an intense blue develops.

Balancing equations.—When there is simultaneous exchange of electrons and protons it may be difficult to balance the reaction equations. A simple method is to decompose the system into two parts, and to equilibrate first the electron exchange, then the exchange of the other ions, O^{2-} and then H^+, which remain in the same state of oxidation during the reaction.

Examples.—(*a*) Permanganate oxidizes ferrous iron:

$$Mn(VII) + 5e \longrightarrow Mn(II)$$

$$5[Fe(II) - e \longrightarrow Fe(III)]$$

whence $\qquad Mn(VII) + 5Fe(II) \longrightarrow Mn(II) + 5Fe(III)$
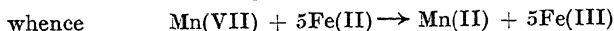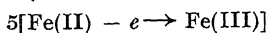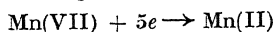
or, introducing the ion which really exists in water, MnO_4^-, then equilibrating O^{2-} and finally H^+:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
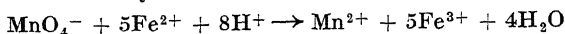
The fact that the equation balances electrically can then be checked.

(*b*) The action of iodate on zinc mercurithiocyanate in the presence of chloride ions can give iodine chloride on the one hand, sulphate and cyanide ions on the other.

$$I^{5+} + 4e \longrightarrow I^+$$

$$CNS^- - 6e \longrightarrow S^{6+} + CN^-$$
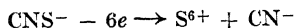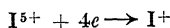
24 electrons must be exchanged:

$$6I^{5+} + 4CNS^- \longrightarrow 6I^+ + 4S^{6+} + 4CN^-$$

whence .

$$6IO_3^- + Zn[Hg(CNS)_4] + 6Cl^- + 8H^+ \longrightarrow$$
$$6ICl + Hg^{2+} + Zn^{2+} + 4SO_4^{2-} + 4HCN + 2H_2O$$
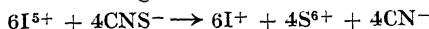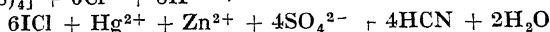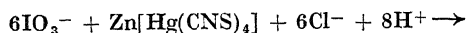
(*c*) The oxidation of alcohol to acetic acid by permanganate.

$$Mn^{7+} + 3e \longrightarrow Mn^{4+}$$

$$C_2H_5OH \longrightarrow CH_3CO_2H$$

$$[C_2]^{4+} - 4e \longrightarrow [C_2]^0$$

whence

$$4MnO_4^- + 3C_2H_5OH + H^+ \longrightarrow 4MnO_2 + 3CH_3CO_2^- + 5H_2O$$
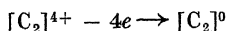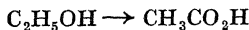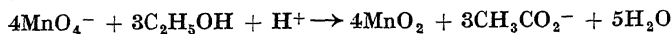
The action of air and water

(*a*) Water can play the part of an oxidant:

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow$$

or $\qquad 2H_2O + 2e \rightleftharpoons H_2 \uparrow + 2OH^-$
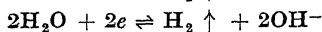
with $\qquad E = E_0 + 0.03 \log \dfrac{|\,H^+\,|^2}{|\,H_2\,|}$

We have seen that the reaction is extremely slow in the absence of catalysts; in practice it is negligible, except with energetic reductants: the latter liberate hydrogen:

$$2Na \downarrow + 2H^+ \longrightarrow 2Na^+ + H_2 \uparrow$$

even in alkaline solution.

$$Zn \downarrow + 2H^+ \longrightarrow Zn^{2+} + H_2 \uparrow$$
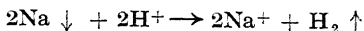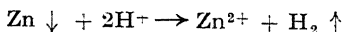
Certain ions are also oxidized with liberation of hydrogen. Thus the chromous salts are converted very slowly to the chromic state:

$$2Cr^{2+} + 2H^+ \longrightarrow 2Cr^{3+} + H_2 \uparrow$$
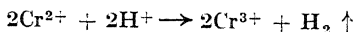
(*b*) Water can play the part of a reductant:

$$2H_2O - 4e \rightleftharpoons 4H^+ + O_2 \uparrow$$

or

$$4OH^- - 4e \rightleftharpoons O_2 \uparrow + 2H_2O$$

or again

$$2O^{2-} - 4e \rightleftharpoons O_2 \uparrow$$
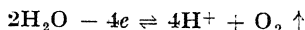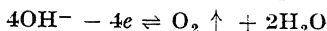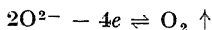
$E = 1 \cdot 23 - 0 \cdot 06$ pH volts when the pressure of oxygen over the solution is 1 atm. But the reaction is very slow. On the other hand, very energetic oxidants react at a considerable rate.

$$2F^- + 2H_2O \longrightarrow 4HF + O_2 \uparrow$$
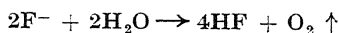
Inversely oxygen, in particular atmospheric oxygen, behaves as an oxidant. The reaction is slow.

$$O_2 \uparrow + 4H^+ + 4Fe^{2+} \longrightarrow 2H_2O + 4Fe^{3+}$$
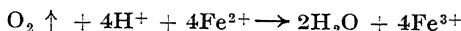
Iodides, etc., are also oxidized.

Water limits the potentials on the oxidizing and reducing sides: the over-energetic oxidants and reductants react with water and, as a result, do not exist in aqueous solution or do so for only a short time.

We shall see that disproportionation reactions can cause the disappearance of certain oxidation states.

Variations of pH during oxidation-reduction reactions

Inversely, oxidation-reduction reactions can cause changes of pH.

Examples.—(*a*) Arsenious acid can be oxidized by iodine in weak alkaline solution.

$$HAsO_2 + I_2 + 2H_2O \longrightarrow HAsO_4^{2-} + 2I^- + 4H^+$$
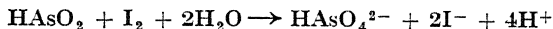
The solution becomes more acid.

Take a solution of arsenite and add acid to it until the red coloration of phenolphthalein commences to decrease in intensity. Oxidize the solution with iodine: the phenolphthalein decolorizes, showing that the pH changes during oxidation.

(*b*) Iodate can be reduced by thiosulphate ions, $S_2O_3^{2-}$, in the course of which protons are used up:

$$IO_3^- + 6H^+ + 6S_2O_3^{2-} \longrightarrow I^- + 3H_2O + 3S_4O_6^{2-}$$
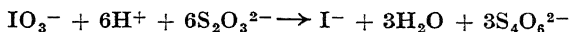
The following experiment can be made: add a drop of methyl orange to a solution of iodate; methyl orange is red in acid, and yellow in less acid solution. Add now a drop of acid. The M.O. becomes red, because IO_3^- is practically non-basic (HIO_3 is a strong acid).

Carry out the same operation with $S_2O_3^{2-}$ in another test-tube; the

same thing is found, because $S_2O_3{}^{2-}$ is also a very weak base ($HS_2O_3{}^-$ is a strong acid).

Mix the two solutions; the M.O. turns yellow on account of the disappearance of the H^+ ions during the oxidation-reduction reaction.

Disproportionation under the influence of pH

Consider the oxidation-reduction systems of chlorine:

$$Cl^- - e \rightleftharpoons Cl^0 \quad \text{and} \quad Cl^0 - e \rightleftharpoons Cl^+$$

The corresponding disproportionation equilibrium is

$$Cl_2 \rightleftharpoons Cl^- + Cl^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Cl^+ is an acid; $Cl^+ + H_2O \rightarrow HClO + H^+$.

As a result, when the pH increases, Cl^+ disappears (even in very acid solution) to be replaced by HClO: the equilibrium (I) is displaced to the right; Cl_2 disproportionates. When the pH has increased sufficiently, there is practically no Cl_2 left in solution. It can thus be said that the formation of the complex HClO stabilizes chlorine in the state of oxidation I^+ and prevents it from existing in the next state (0).

Quantitatively, we have the following relations:

$$E = 1 \cdot 4 + 0 \cdot 03 \log \frac{|\,Cl_2\,|}{|\,Cl^-\,|^2} \text{ volts}$$

$$E = E_1 + 0 \cdot 03 \log \frac{|\,Cl^+\,|^2}{|\,Cl_2\,|} \quad \text{and} \quad \frac{|\,HClO\,| \cdot |\,H^+\,|}{|\,Cl^+\,|} = K_1$$

whence

$$E = E_1 - 0 \cdot 06 \log K_1 + 0 \cdot 03 \log \frac{|\,HClO\,|^2 \cdot |\,H^+\,|^2}{|\,Cl_2\,|}$$

$$= 1 \cdot 6 + 0 \cdot 03 \log \frac{|\,HClO\,|^2 \cdot |\,H^+\,|^2}{|\,Cl_2\,|}$$

$$= 1 \cdot 6 - 0 \cdot 06\, p\text{H} + 0 \cdot 03 \log \frac{|\,HClO\,|^2}{|\,Cl^2\,|} \text{ volts}$$

system: $2HClO + 2H^+ + 2e \rightleftharpoons Cl_2 + 2H_2O$

The normal potentials of the two systems as a function of pH are shown in fig. 11.

FIG. 11.—FORMAL NORMAL POTENTIALS OF THE SYSTEMS $Cl(I)/Cl(O)/Cl^-$ AS A FUNCTION OF pH

It can be seen from this figure that at pH 0, for $E < 1.4$ volts, there is more Cl^- than Cl_2; at $E = 1.4$ volts, $| Cl_2 | = | Cl^- |^2$; for $E < 1.6$ volts, HClO predominates. When the pH increases, the region in which Cl_2 predominates is restricted. For $pH < 3.3$, HClO reacts with Cl^- to give Cl_2 until Cl_2 more or less predominates. At $pH = 3.3$,

$$| HClO |^2 = | Cl_2 | = | Cl^- |^2$$

We then have

$$E = 1.4 + 0.03 \log \frac{| Cl_2 |}{| Cl^- |} = 1.6 + 0.03 \log \frac{| HClO |^2 | H^+ |^2}{| Cl_2 |} \text{ volt}$$

whence $pH = 3.3$.

Above pH 3.3, the formal normal potential of the system $HClO/Cl_2$ becomes less than that of the system Cl_2/Cl^-; as a result, if chlorine is dissolved in an aqueous solution, the oxidant Cl_2 of the second system will react, partially at least, with the reductant Cl_2 of the first, giving HClO and Cl^-; Cl_2 disproportionates. For $pH = 3.3$, HClO and Cl^- will predominate in the solution, and we shall then have the system:

$$HClO + H^+ + 2e \rightleftharpoons Cl^- + H_2O$$
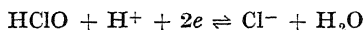
with
$$E = E'_0 + 0.03 \log \frac{| HClO |.| H^+ |}{| Cl^- |}$$

A simple calculation gives

$$E'_0 = \frac{1.6 + 1.4}{2} = 1.5 \text{ volts}$$

thus
$$E = 1.5 + 0.03 \log \frac{| HClO |.| H^+ |}{| Cl^- |} \text{ volts}$$

If the pH be increased still further, the concentration of chlorine becomes very small. It can easily be calculated that at pH 6, for

$$| HClO | = | Cl^- | = 10^{-2}M, \quad | Cl_2 | = 10^{-5}M$$

There is practically no chlorine left in solution.

Note.—HClO is an acid of $pK = 7.3$. Above pH 7.3, the system $ClO^- + 2H^+ + 2e \rightleftharpoons Cl^- + H_2O$ (fig. 11) is set up.

Corollary.—Above pH 6, HClO or of ClO^- cannot be reduced to Cl_2: Cl^- is obtained directly. Inversely, oxidation of Cl^- gives HClO or ClO^-.

Other examples.—In the course of oxidation or reduction reactions, the intermediate compounds disproportionate and, as a result, they remain unobservable if the rate of disproportionation is sufficient.

Thus, the thiocyanate ion is oxidized in acid solution as follows:

$$6CNS^- - 6e \longrightarrow 3(CNS)_2 \quad \text{oxidation}$$
$$3(CNS)_2 + 4H_2O \longrightarrow SO_4{}^{2-} + 5CNS^- + 8H^+ + CN^- \quad \text{overall disproportionation}$$

$$CNS^- + 6e + 4H_2O \longrightarrow SO_4{}^{2-} + CN^- + 8H^+ \quad \text{overall system}$$
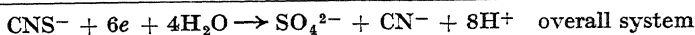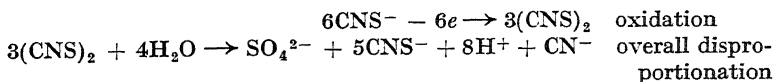
It may be important to distinguish the two phases of the reaction.

The intermediate states of oxidation Cr(V), Cr(IV), etc., are unknown, because of disproportionation reactions.

Experiment.—Iodine I_2 is disproportionated in alkaline solution:

$$I_2 + OH^- \rightleftharpoons HIO + I^-$$
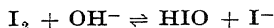
Add caustic soda to a solution of iodine; the brown iodine colour disappears.

Influence of disproportionation on pH.—When chlorine is added to an alkaline solution, the disproportionation reaction

$$Cl_2 + H_2O \rightleftharpoons ClO^- + Cl^- + 2H^+$$
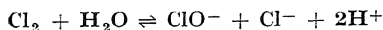
occurs. The solution becomes gradually less alkaline and the disproportionation can then stop.

Normal potentials (in volts)
(Ion and electron exchanges)

$$2HSO_3^- + 2H^+ + \quad 2e \rightleftharpoons S_2O_4^{2-} + 2H_2O \quad . \quad . \; + 0\cdot07 \text{ volt}$$

$$TiOOH^+ + H^+ + \quad e \rightleftharpoons TiO^+ + H_2O. \quad . \quad . \; + 0\cdot03 \quad ,,$$

$$NO_3^- + 3H^+ + \quad 2e \rightleftharpoons HNO_2 + H_2O \quad . \quad . \; + 0\cdot93 \quad ,,$$

$$HNO_2 + H^+ + \quad e \rightleftharpoons NO + H_2O \quad . \quad . \quad . \; + 0\cdot98 \text{ for 1 atm. pressure of NO}$$

$$VO_2^+ + 2H^+ + \quad e \rightleftharpoons VO^{2+} + H_2O \quad . \quad . \quad 1\cdot00 \text{ volt}$$

$$Cr_2O_7^{2-} + 14H^+ + \quad 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \quad . \quad . \quad 1\cdot36 \quad ,,$$

$$IO_3^- + 6H^+ + \quad 6e \rightleftharpoons I^- + 3H_2O \quad . \quad . \quad . \quad 1\cdot08 \text{ (calculated)}$$

$$O_2 + 4H^+ + \quad 4e \rightleftharpoons 2H_2O \quad . \quad . \quad . \quad . \quad 1\cdot23 \text{ for 1 atm. pressure of } O_2$$

$$2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O \quad . \quad . \quad . \quad 1\cdot48 \text{ volt}$$

$$ClO_3^- + 6H^+ + \quad 6e \rightleftharpoons Cl^- + 3H_2O \quad . \quad . \quad . \quad 1\cdot45 \text{ (calculated)}$$

$$O_3 + 2H^+ + \quad 2e \rightleftharpoons O_2 + H_2O \quad . \quad . \quad . \quad 2\cdot07 \qquad ,,$$

CHAPTER IX

PROPERTIES OF PRECIPITATES

ADSORPTION.—In solids, the molecules, atoms, or ions occupy definite positions relative to one another. Take for example the crystal of silver chloride. It has a very simple crystal lattice (cubic system) consisting of a regular arrangement of Ag^+ and Cl^- ions. One Ag^+ ion is surrounded in space by six Cl^- ions, and each Cl^- ion is surrounded by six Ag^+ ions. Figs. 12 and 13 show plan views of the structure. In the interior of the crystal the electrostatic forces balance one another and ensure the stability of the crystal lattice. But at the surface, on the other hand, these attractions are not balanced and make themselves evident, particularly at the corners and edges of the crystal. (The effect is similar to that which produces a surface tension at the interface between a liquid and another liquid, solid, or gas.)

K^+		K^+			NO_3^-		NO_3^-	
Cl^-		Cl^-			Ag^+		Ag^+	
Ag^+	Cl^-	Ag^+	Cl^-		Ag^+	Cl^-	Ag^+	Cl^-
Cl^-	Ag^+	Cl^-	Ag^+		Cl^-	Ag^+	Cl^-	Ag^+
Ag^+	Cl^-	Ag^+	Cl^-		Ag^+	Cl^-	Ag^+	Cl^-
Cl^-	Ag^+	Cl^-	Ag^+		Cl^-	Ag^+	Cl^-	Ag^+
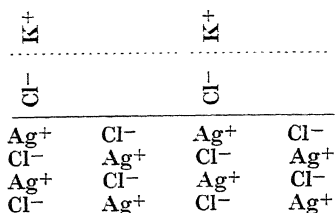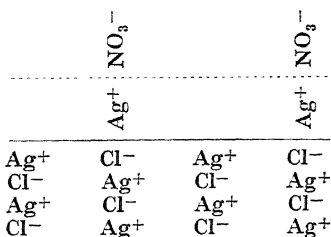
FIG. 12   FIG. 13

As a result of this unbalance of electrostatic attractions at the surface, ions present in the solution can be attracted to it as shown in the figures above. This is the phenomenon of adsorption.

The Cl^- ions in fig. 12 and the Ag^+ ions in fig. 13 are adsorbed. In the liquid surrounding the crystal, these ions experience a force attracting them to the surface and are found fixed on the solid if it is separated from the solution.

It is customary to represent this state of affairs by the scheme:

$$ClAgCl^- \mid K^+ \quad \text{and} \quad AgClAg^+ \mid NO_3^-$$
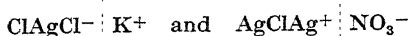
Notes.—(1) A precipitate preferentially adsorbs its own ions as though the crystal were continuing to grow. Thus a precipitate of silver chloride will adsorb Cl^- ions in preference to other anions, if it is immersed in a solution of an alkali chloride.

(2) The adsorption increases with the charge on the ions: ions with several charges are more easily adsorbed.

(3) Adsorption increases with the concentration of the ion under consideration. In principle $a = kc^{1/n}$, a being the quantity adsorbed, c the concentration, in the solution, n an exponent greater than unity.

(4) Polar molecules are also adsorbed.

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Dimensions of particles

1 micron $= 1\,\mu = 10^{-6}$ metre

Proton: $10^{-12}\,\mu$.
Atomic nuclei: $10^{-9}\,\mu$.
Electron: $2.10^{-9}\,\mu$.
Non-solvated molecules and ions: 10^{-3}–$10^{-4}\,\mu$, macromolecules up to 0·28 μ.

Colloids: $\begin{cases} 10^{-3}\,\mu \\ 10^{-2}\,\mu \\ 10^{-1}\,\mu \end{cases}$ ultramicroscope, pores of ultrafilters.

Crystals visible to the naked eye: $\begin{cases} 0\cdot25\,\mu \\ 1\,\mu \end{cases}$ microscope, pores of ordinary filters.

COLLOIDS

The term 'colloidal' is applied to a phase composed of particles so small that the forces at its surface play an important part in determining its properties.

The dimensions of colloidal particles are 10^{-1} to $10^{-3}\,\mu$. These particles are in general built up by the association of molecules or small charged crystals and they are stabilized in solution by adsorption of ions so that they are separated from the solution by a double layer (fig. 14). They can only increase in size very slowly on account of the charges they carry.

These associations of molecules or ions are called 'micelles'.
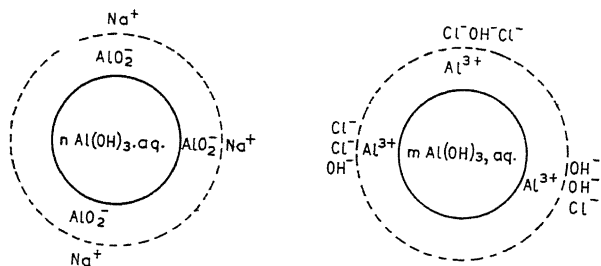
FIGS. 14 AND 15.—MICELLES OF ALUMINIUM HYDROXIDE
IN ALKALI AND ACID

Examples.—Aluminium hydroxide is charged positively at pH < 8 (fig. 15) and negatively at pH > 8 (fig. 14).

Properties.—(1) They pass through or clog ordinary filters. They can be separated by means of ultrafilters (collodion, parchment).

(2) When the particles attain a size of $10^{-2}\,\mu$ their solutions appear cloudy by reflected light, and clear by transmitted light (Tyndall effect). The particles can be seen by diffraction of light in the ultramicroscope.

(3) The molecular weight of the particles can be very high, as a result of the association of a large number of molecules: thus with silica, 50,000; ferric hydroxide, 3000 to 8000.

Charges on colloidal particles

The charge on a colloidal particle depends essentially on the medium. Thus the majority of hydroxides adsorb cations (including H^+) in acid solution and thus become positively charged; they fix anions (including OH^-) in sufficiently alkaline solution and thus become negatively charged.

Flocculation, peptization.—If a colloid is discharged, that is to say if the double layer be destroyed in some way, the particles cease to repel one another, and precipitation occurs: this is called 'flocculation'. Experience shows that this result can be obtained by the addition of suitable ions to the solution.

The charge of the flocculating ion is extremely important; the higher the charge, the greater the flocculating power, and the less electrolyte has to be added.

Example.—Flocculation of arsenic sulphide.

If 500 cations carrying a single charge (e.g. K^+) are required in order to flocculate a given colloidal solution of arsenic sulphide, only 10 cations carrying double charges are required (e.g. Mg^{2+}) and only 1 of a cation having a triple positive charge (e.g. Al^{3+}).

During washing, precipitates can revert to the colloidal state, and this phenomenon is known as 'peptization'. It is therefore a good idea to wash a precipitate with a suitable electrolyte, to prevent this happening: e.g. silver chloride with nitric acid, and nickel sulphide with a solution containing ammonium ions.

Sometimes the precipitate 'ages' and is then no longer susceptible to being peptized.

Hydrophilic colloids.—Certain colloids have the property of adsorbing water molecules, sometimes in large quantity. The liquid can become quite viscous. Flocculation gives gels which are difficult to wash and sometimes difficult to dehydrate completely, even on calcination (silica, alumina, stannic hydroxide, etc.).

FORMATION AND AGEING OF PRECIPITATES

The formation and transformation of precipitates towards stable equilibrium is rarely a rapid or instantaneous process. It is therefore necessary to study the phenomena as a function of time.

Formation of nuclei.—Precipitation commences with the formation of crystalline nuclei as a result of the association of certain ions, for example Ag^+ and Cl^-. These nuclei grow by adding on new Ag^+ and Cl^- ions. The more concentrated the solution, and the less soluble the compound, the more numerous are the nuclei formed in a given space of time.

When the formation of nuclei is slow, which frequently happens, 'supersaturation' is said to occur. The formation of nuclei can be accelerated by agitation, by scratching the sides of the vessel so as to create some sharp corners which promote the adsorption of ions which can serve as the starting-points for the growth of a crystal, and by introducing into the solution crystals which have already been formed.

Growth of crystals.—Two factors affect the growth of crystals:

(1) The frequency with which new ions arrive at the surface of the

6

crystal already formed. This frequency is greater the larger the concentration of the relevant ion in the solution. The nuclei have a tendency to grow more quickly the larger the concentrations of the ions of interest. Agitation which transports a large amount of solution to the nuclei promotes the growth of the crystals.

(2) The rate at which the ions arrange themselves in the crystal lattice. This rate is large with polar compounds such as $AgCl$, $BaSO_4$, and low with the hydroxides such as $Th(OH)_4$, $Ti(OH)_4$, etc.

If the effect of the first factor is predominant, the nuclei grow irregularly and very irregular crystals are obtained, which contain cavities and, as a result, have a very large surface (porous crystals).

On the other hand, if the second factor is preponderant, the crystals will be perfect.

$AgCl$, $Mg(OH)_2$ easily give perfect crystals.

The fewer nuclei there are at the start, the fewer will be the number of crystals formed, and the slower will be the rate of precipitation. If there are plenty of nuclei, for instance when two concentrated solutions are rapidly mixed, precipitation is very rapid, and crystals are very small and imperfect.

Example.—Precipitation of barium sulphate by mixing together rapidly solutions of a sulphate and a barium salt.

In 3·7M solution (of the reagents) the solution sets to a gelatinous mass. The individual particles cannot even be seen in the ultramicroscope.

In 0·75–3·0M solution, the precipitate is colloidal, but the particles can be seen in an ultramicroscope having a magnification of 1500.

In 0·005–0·05M solution, crystals are obtained.

In 0·001M solution, the mixture remains clear for about 5 minutes, then becomes opalescent and precipitates at the end of about 2 hours. Crystals 5 μ in size.

When the solutions are 0·0002M, it is necessary to wait a month for precipitation, and the crystals obtained are 15 μ in size.

Ageing of precipitates.—Variations in their solubility.—The surface and even the interior of crystals are the seat of a constant interchange of ions with the solution. When the system is far from equilibrium, the quantity of ions which are fixed in the crystal is larger than that which leaves it. This exchange tends finally to an equilibrium between a perfect crystal and a saturated solution. In particular, every ion which is incorrectly located in the crystal lattice has a greater tendency to leave than one correctly placed; it is more active, and its 'solubility' is greater. The result is that little by little the crystal becomes more perfect and its solubility diminishes. Small crystals have more numerous active points (edges and corners) and are therefore more active; they are more soluble than large crystals; they dissolve more quickly, and finally, by and large, the average size of the crystals increases with time.

Amorphous precipitates tend to become crystalline, imperfect crystals to perfect themselves, their size to increase, and their solubility to decrease.

This process is generally referred to as 'ageing' or 'development'.

It can be seen from fig. 16 that the solubility varies very little once the size of the crystals becomes large. This in general occurs for particles,

assumed spherical, 1–2 μ and larger in diameter. On the other hand, the solubility changes very rapidly for very small crystals.

Example.—Magnesium hydroxide $Mg(OH)_2$ has a solubility which can decrease in the course of 24 hours from $10^{-3}M$ to $10^{-4}M$.

Notes.—(1) This rule gives only qualitative indications because, in practical cases, it is not at all easy to determine the surface of very small crystals, particularly those that are porous or agglomerated.

(2) Other phenomena can also cause the solubility to vary: spontaneous dehydration of the precipitate and transformation into a more stable crystalline modification. In all cases, the solubility diminishes.

Rate of transformations.—When the compounds have only a very small solubility, or when the crystals are large or perfect (natural compounds for example), the exchanges are slow and the crystals only grow at an infinitely slow rate. Thus numerous precipitates remain amorphous, $Th(OH)_4$ for example; small crystals of $BaSO_4$ of 0.2 μ practically cease to grow under certain conditions.
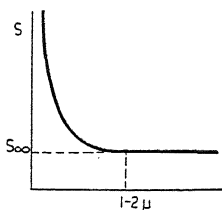
FIG. 16
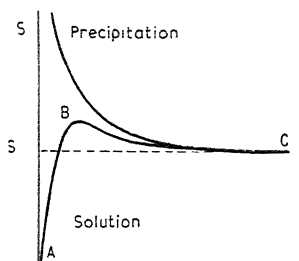
FIG. 17.—APPARENT SOLUBILITY OF $CaSO_4$ AS A FUNCTION OF TIME

Certain substances, such as sodium hexametaphosphate for example, can slow down or stop these phenomena of development of crystals.

Influence of temperature.—Raising the temperature enormously increases all the rates of formation of nuclei, of rearrangement and growth of crystals.

Dissolution of a precipitate.—The smallest particles which are the more soluble dissolve first, then the larger particles which remain gradually grow and the solubility then decreases.

Example.—If calcium sulphate, $CaSO_4 . 2H_2O$, finely ground, be introduced into water, then the solubility curve as a function of time follows the course indicated in fig. 17. Along the part AB, the solution is not yet saturated, and sulphate dissolves; at B, the solution is saturated with respect to small particles, and along BC the particle size is growing and the solubility decreasing.

COLOUR AND SIZE OF PRECIPITATES.—The colour of coloured precipitates depends on the dimensions of their particles.

Example.—Antimony sulphide is yellow in the colloidal state; precipitated in neutral or slightly acid solution, it is orange. If it is precipitated in very acid solution, its solubility is greater, the precipitation

is slower and the crystals are larger: it is then black, like the natural sulphide stibnite.

Gold can be precipitated as pink, purple, or brown according to the size of its particles.

IMPURITIES IN PRECIPITATES

ADSORPTION.—Precipitates contain impurities as a result of adsorption. The larger the surface of the precipitates, the more imperfect the crystals, the more marked are the phenomena of adsorption. Colloidal precipitates are particularly impure, generally containing residual material from the double layer which stabilized the micelles when in solution.

In analytical chemistry, it is necessary to get precipitates as pure as possible. To do this, conditions are created which promote the formation of crystals as large and as perfect as possible. This is achieved by performing precipitation in dilute solutions, by ageing the precipitates by leaving them for long enough in contact with the solution, by adjustment and maintenance of the temperature, by the addition of compounds which are preferentially adsorbed and can later be easily removed, e.g. by ignition, and by suitable washing of the precipitates.

The redissolution after filtration, and reprecipitation of a compound of low solubility, in general decreases the adsorption, because the quantity of adsorbed ion is a function of its concentration in solution.

Post-precipitation.—The precipitation of certain compounds, which is generally very slow on account of supersaturation, can be accelerated by the presence of other precipitates which, by adsorption, promote the formation of crystals.

Thus ZnS in $0 \cdot 1$N-HCl does not precipitate or does so extremely slowly. CuS, HgS cause it to be precipitated after some time.

EXAMPLES OF APPLICATION IN ANALYTICAL CHEMISTRY

The main object is to obtain precipitates which are easy to centrifuge or to filter and as pure as possible. Precipitation can also be utilized for carrying down and thus separating traces of elements.

Precipitation of silver chloride for the gravimetric determination of silver.—The precipitate of silver chloride obtained in the presence of an excess of KCl adsorbs its Cl^- ions, then the cations, mainly K^+:

$$ClAgCl^- \mid K^+$$
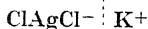
Prolonged washing of the precipitate with dilute nitric acid gradually replaces the K^+ ion by H^+:

$$ClAgCl^- \mid H^+$$
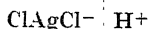
HCl is volatilized in drying the precipitate and pure AgCl is finally obtained.

Separation of aluminium from divalent elements.—When

$Al(OH)_3$ is precipitated towards pH 8 with ammonia, it is negatively charged and adsorbs cations, mainly those whose charge is high: Zn^{2+}, Mg^{2+}, etc. This adsorption can be partially inhibited by the addition of a large amount of ammonium chloride: this is then adsorbed preferentially, and can be driven off afterwards during calcination.

Solubility of nickel sulphide.—When the particles of this compound increase in size, its solubility decreases.

Thus nickel sulphide has a solubility product which can change from $5 \cdot 10^{-11}$ to 10^{-16}. It does not precipitate unless the pH is above 4·5, but the precipitate ages rapidly, and can then not be redissolved even at pH < 0.

Precipitation of zinc sulphide.—Zinc sulphide, a salt of a weak acid, is more soluble in acid than in alkaline solution, so that the particles formed during the precipitation are larger in acid solution. Thus the precipitate obtained in ammoniacal solution is difficult to filter, even after flocculating the colloid. Precipitated in a formate buffer of pH 3·0, zinc sulphide is obtained in much larger particles, much more easy to filter.

Precipitation of the alkaline earth salts.—The precipitation of the majority of the low-solubility alkaline earth salts is slow. Thus, at ordinary temperature, calcium carbonate takes a long time to come down, and the same is true of its sulphate. Magnesium hydroxide takes several days to come down completely.

Raising the temperature speeds up these precipitations.

Precipitation of ammonium magnesium phosphate.—Ammonium magnesium phosphate $MgNH_4PO_4 \cdot 6H_2O$ is used in quantitative analysis. It is soluble in acids, but only slightly soluble in alkaline solution. Only a few nuclei are formed in acid solution. The reagents containing Mg^{2+}, PO_4^{3-}, and NH_4^+ are mixed in acid solution; the mixture is only then neutralized with ammonia of which a large excess is finally added in order to decrease the solubility of the compound. Twelve hours have to be allowed for complete precipitation. Complete precipitation with sufficiently large crystals can be attained, however, in considerably less time, 10 to 30 minutes, by mechanical agitation or by bubbling a stream of air through the mixture.

Applications of adsorption.—(1) Adsorption can be used for carrying down and thus separating traces of elements, for example Pb^{2+} by $CaCO_3$. This technique finds numerous applications in radio-chemistry.

(2) The phenomenon of adsorption of dyes is used in qualitative analysis for detecting certain molecules, and in quantitative analysis for detecting the end-point of some reactions.

Precipitation of hydroxides.—A large number of hydroxides are only slightly soluble, in particular those which correspond to metals in a high state of oxidation: $Si(OH)_4$, $Zr(OH)_4$, $Nb(OH)_5$, $Ta(OH)_5$, etc. Even the hydroxides of II^+ and III^+ oxidation number frequently precipitate in the colloidal form, e.g. $Be(OH)_2$, $Cr(OH)_3$, etc. Certain of these are, however, crystalline, $Mg(OH)_2$ for example.

These colloids are flocculated either with H^+ ions when they are only slightly soluble in acid solution: tungstic acid, silica; or by NH_4^+ ions, or by gelatine.

Precipitated hydroxides are rarely pure, because of adsorption.

Boiling the hydroxides in the presence of the mother liquors frequently transforms them into a less soluble form, either as a result of the growth of the particles, or by dehydration (or both).

The hydroxides of the heavy metals are easily dehydrated by boiling them in contact with the solutions from which they have been precipitated, or the transformation may easily take place spontaneously: AgOH gives Ag_2O, $Hg(OH)_2$ gives HgO, and so on.

The precipitation of hydroxides is frequently accompanied by the formation of basic salts.

Phenomena which accompany the precipitation of hydroxides in general.—Neutralization of a solution of Al^{3+},aq. results in the formation of basic ions such as $AlOH^{2+}$. These basic ions generally condense slowly in the course of time:

$$2Al(OH)^{2+} \rightleftharpoons Al_2(OH)_2^{4+}$$
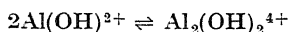
These condensations are accompanied by dehydration, then by the loss of H^+. In this way the condensed ions become gradually larger and their formulae approach closer and closer to that of the hydroxide. There is then no distinction between these ions and the micelles which were described and defined on page 66. Finally flocculation occurs. The region of transition between the simple ion (Al^{3+}) and the flocculation of the hydroxide ($Al(OH)_3$) is smaller or larger depending upon the conditions of operation and the nature of the element.

Thus, under certain conditions 2·5 OH^- can be added for each Al^{3+} without forming a precipitate of the hydroxide.

The phenomenon is the more important the higher the state of oxidation. Thus with a hydroxide like $Mg(OH)_2$ it is difficult to detect the intermediate compounds. On the other hand, it is difficult to get flocculation of $Nb(OH)_5$ at all.

After the hydroxide has been flocculated, it generally continues to develop, its solubility decreases, sometimes considerably, particularly when the system is kept hot.

Redissolution in acid is accompanied in principle by similar phenomena, with a certain amount of hysteresis ('olation').

Thus aluminium hydroxide, which is precipitated at around pH 5, does not redissolve at any considerable rate until the pH is reduced to around 0.

The redissolution commences with the passage of the precipitate into the colloidal state, then the dimensions of the micelles diminish and as a result the ratio $Al^{3+}/Al(OH)_3$ in solution increases and finally the solution only contains cations.

In a similar manner the redissolution of a hydroxide to the anionic state in alkaline solution is accompanied by the preliminary formation of a colloid which gradually passes over into anions.

Thus we have, depending on the pH, $Al^{3+}+AlOH^{2+}$, $Al_m(OH)_n^{(3m-n)+}$ or $pAl(OH)_3.qAl^{3+}$, $Al(OH)_3 \downarrow$, $rAl(OH)_3.sAlO_2^-$ or $Al_t(OH)_u^{b-}$.

Boiling the solutions causes hydroxides to age and if the solutions are not sufficiently acid or alkaline to have nothing but ions present, the state of the solution is displaced towards that for the precipitation of the aged hydroxides, which do not redissolve again on cooling the solution.

Similar phenomena are produced over a longer period of time at lower temperatures.

The solutions of aluminates can reproduce a precipitate of a very low solubility hydroxide, if the solution is not sufficiently alkaline.

All these phenomena occur with very many hydroxides.

Action of hydroxylated acids.—Certain hydroxylated organic acids, such as citric, tartaric, etc., have the property of maintaining the hydroxides in the form of extremely fine particles which can pass through ordinary filters, quite independent of the formation of complexes.

Lakes.—The colloidal particles of a hydroxide (or the large condensed ions which are their equivalent) have very strongly marked adsorptive properties particularly for dyes or combinations of dyes and ions. This adsorption is accompanied by changes of colour which are in certain cases characteristic (see adsorption reagents, p. 122).

Induced precipitation.—Certain isomorphous substances are capable of co-precipitating in mixed crystals, at least within certain proportions. This occurs with the mercurithiocyanates of Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+} (p. 187). In dilute solution, the precipitation of one of these salts may be on occasion very slow: sometimes infinitely slow. The addition of one of these other ions can accelerate the rate of precipitation; mixed crystals form immediately, thus increasing the sensitivity of the first salt to precipitation.

CHAPTER X

SOLUBILITY OF SLIGHTLY SOLUBLE COMPOUNDS

Precipitation reactions.—When sodium chloride and silver nitrate are allowed to interact, the Ag^+ ions and the Cl^- ions react in order to produce low-solubility silver chloride which precipitates. The NO_3^- ions and the Na^+ ions do not take part in the reaction. We have

$$Ag^+ + Cl^- \longrightarrow AgCl \downarrow$$
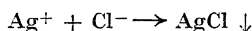
Solubility product.* —Consider a slightly soluble compound BA. In solution there is a small concentration of B^+ and A^- ions in equilibrium with the ions in the solid.
We have
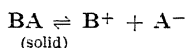
$$BA \rightleftharpoons B^+ + A^-$$
$$\text{(solid)}$$

When equilibrium is reached

$$\frac{|\,B^+\,|.|\,A^-\,|}{|\,BA\,|} = K$$

Since solid is present, the activity of BA is constant, and we have

$$|\,B^+\,|.|\,A^-\,| = s$$

s is called the 'solubility product'. For a given temperature it is constant, if equilibrium exists between the solid and the solution.
With a compound B_mA_n we have

$$|\,B\,|^m.|\,A\,|^n = s$$

Examples.—The solubility product of silver chloride is given by the relation $|\,Ag^+\,|.|\,Cl^-\,| = 10^{-9.7}$
With silver chromate, Ag^2CrO_4, we have $|\,Ag^+\,|^2.|\,CrO_4{}^{2-}\,| = 10^{-11.4}$.
With antimony sulphide, Sb_2S_3: $|\,Sb^{3+}\,|^2.|\,S^{2-}\,|^3 = 10^{-24}$.
Precipitation by an excess of reagent.—When chloride ions are introduced into a solution of silver ions, silver chloride precipitates and the silver solubility is

$$S = |\,Ag^+\,| = \frac{s}{|\,Cl^-\,|}$$

Increase in the activity of the Cl^- ions decreases the activity of the Ag^+ ions in the solution. The precipitation of silver is the more complete the greater the excess of chloride ions.

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*Frequently abbreviated to 's.p.'
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Some apparent solubility products as a function of the ionic strength

The term 'apparent solubility product' is applied to the solubility product obtained with concentrations, not activities.

The table below gives the values of the exponent n, when the solubility product is expressed in the form 10^{-n}.

$\sqrt{I}$:	0	0·25	0·50
$PbSO_4$	7·7	6·85	6·45
$BaCrO_4$	9·85	9·05	8·6
$AgBr$	12·2	12·05	11·9
$Ba(IO_3)_2$	8·9	8·2	7·7
Hg_2Cl_2	18·0	17·4	17·0

PRECIPITATION AND ACIDITY

SOLUBILITY OF HYDROXIDES AS A FUNCTION OF pH

FOR a slightly soluble hydroxide MOH there are in principle two equilibria:

$$MOH \downarrow \rightleftharpoons M^+ + OH^- \quad \text{with} \quad s_1 = |\,M^+\,|\,|\,OH^-\,|$$

or

$$|\,M^+\,| = \frac{s_1}{|\,OH^-\,|} = \frac{s_1\,|\,H^+\,|}{K_{H_2O}}$$

and

$$MOH \downarrow \rightleftharpoons MO^- + H^+ \quad \text{with} \quad s_2 = |\,MO^-\,|\,|\,H^+\,|$$
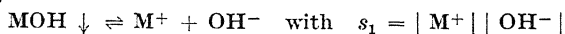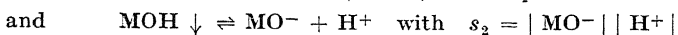
or

$$|\,MO^-\,| = \frac{s_2}{|\,H^+\,|}$$

The solubility S of the hydroxide is given by

$$S = |\,M^+\,| + |\,MO^-\,|$$

where

$$S = K\,|\,H^+\,| + \frac{K'}{|\,H^+\,|} = K.10^{-p\mathrm{H}} + K'.10^{p\mathrm{H}}$$

This applies when the solution is saturated, that is, when there is solid in contact with it.

S varies with pH in the manner shown in the curve shown below (fig. 18). Along the left branch it varies as $K.10^{-p\mathrm{H}}$ and along the right branch as $K'.10^{p\mathrm{H}}$. The two branches are exponential functions. In the case shown here, S varies by a factor of ten for unit change of pH.
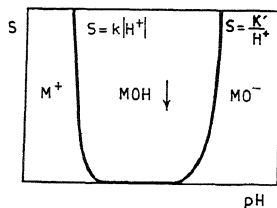
FIG. 18.—APPARENT SOLUBILITY OF THE HYDROXIDE MOH
AS A FUNCTION OF pH

Form of the solubility curve.—For the hydroxide MOH, the solubility in acid solution is given by

$$|\,M^+\,|.|\,OH^-\,| = s$$

whence

$$|\,M^+\,| = K\,|\,H^+\,|$$

For the hydroxide $M(OH)_n$ we have

$$|\,M^{n+}\,|.|\,OH^-\,|^n = s'$$

whence

$$|\,M^{n+}\,| = K'.|\,H^+\,|^n$$

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Since $\log S = f(pH)$ a plot of $\log S$ against pH will give two straight lines, as shown in fig. 19.
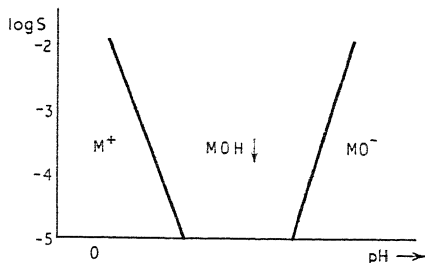
FIG. 19.—LOG OF APPARENT SOLUBILITY OF A HYDROXIDE
AS A FUNCTION OF pH

Example.—Aluminium hydroxide $Al(OH)_3$ can give the anions AlO_2^- and the cations Al^{3+}. Its solubility curve as a function of pH is given here (fig. 20). The precipitation pH's of $M/100$ solution are given by $|Al^{3+}|.|OH^-|^3 = 10^{-32\cdot7}$ and $|AlO_2^-|.|H^+| = 10^{-12\cdot6}$ to 10^{-15} with $|Al^{3+}| = 10^{-2}$; thus $3\cdot8$, $10\cdot6$–$13\cdot0$.
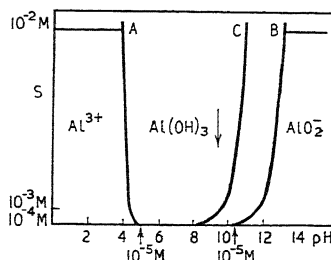
FIG. 20.—APPARENT SOLUBILITY OF ALUMINIUM HYDROXIDE
AS A FUNCTION OF pH

Notes.—We have seen on page 72 that the precipitation of the hydroxides is in general accompanied by complicated phenomena of slow condensation and the formation of colloids. The present method of studying these phenomena is thus simply a formal one, and only to be regarded as a first approximation. This approximation can be improved by indicating the several apparent solubility products, thus giving several solubility curves according to the degree of ageing of the precipitate. Thus for aluminium, we have $|AlO_2^-|.|H^+| = 10^{-12\cdot6}$, for the precipitation of the hydroxide, the most soluble form, and $|AlO_2^-|.|H^+| = 10^{-15}$ for the developed form which corresponds better to the dissolution of the hydroxide.

The basic and condensed ions which are present in solution just prior to the formation of the hydroxide are complicated and little is known about them, and equilibria involving them are not achieved. A reaction equation can be written down as follows, assuming that only simple basic ions are present:

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+; \quad pK = 4\cdot9$$
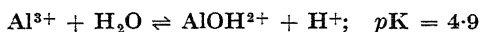
The real state of affairs can be more nearly approached by supposing that simple condensed ions are formed.

These approximations permit in general a sufficiently close approximation to what actually happens. The solubility ought to be calculated on the basis of all these ions which are in solution.

pH of precipitation of hydroxides.—In order to fix the solubility curve for the hydroxides, it is convenient to give the precipitation pH for an 0·01M solution. This is the most usual concentration met with in analytical chemistry. The precipitation of the hydroxide is reckoned to be quantitative if only 1/1000 of the amount initially present remains in solution, i.e. if the solution after precipitation is only 10^{-5}M in the particular metal whose hydroxide is being precipitated. Reagents generally cease to detect ions at this concentration (approx. 1 mg/litre or 1 p.p.m.).

For a hydroxide MOH, precipitation generally takes place over a range of 3 pH units.

for $M(OH)_2$ . . . . . . 1·5 pH units
„ $M(OH)_3$ 1   „   „
„ $M(OH)_4$ . . . . . . 0·75 „   „

Example.—An 0·01M solution of aluminium commences to precipitate at pH 3·8. At pH 4·8, the concentration of the ions Al^{3+} in solution is not more than 10^{-5}M. A solution of aluminate commences to precipitate at pH 10·6; the precipitation is complete when the pH has fallen to pH 7·6. When the hydroxide is developed, it commences to redissolve at pH 10·6 and the dissolution is complete at pH 13·0. Thus, precipitation is 'quantitative' between pH 4·8 and 10·0.

pH of precipitation of the principal hydroxides.—In the following table, the first number indicates the precipitation pH for an 0·01M solution. The second figure is the pH at which the hydroxide redissolves in alkaline solution.

$Si(OH)_4$	< 0	7·5–11	$Ga(OH)_3$.	3·5	9·7–13
$Nb(OH)_5$	< 0	~14	$Al(OH)_3$.	3·8	10·6–13·0
$Ta(OH)_5$	< 0	~14	**$Bi(OH)_3$.	4	> 14
$Pb(OH)_4$	< 0	12–13	$Cr(OH)_3$.	5·0	13–14
H_2WO_4	< 0	~ 8	**$Cu(OH)_2$.	5·0	15·0
$Ti(OH)_4$	0	> 14	$Fe(OH)_2$.	5·8	> 14
$Tl(OH)_3$	0·3	> 14	$Be(OH)_2$.	5·8	13·5
$Co(OH)_3$	0·5	> 14	Rare earths	5·9–8·4	> 14
$Sn(OH)_4$	0·5	12–13	**$Cr(OH)_2$.	6·5	?
$Ce(OH)_4$	~0·8	> 14	**$Zn(OH)_2$.	6·8	13·5
$Zr(OH)_4$	~1	> 14	$Ce(OH)_3$.	7·1–7·4	> 14
SbO_2H .	?	8·9	$Pb(OH)_2$.	7·2	13
$Sn(OH)_2$	1·5	13	**$Ni(OH)_2$.	7·4	> 14
HgO	2	> 14	**$Co(OH)_2$.	7·5	> 14
$Fe(OH)_3$	2·2	> 14	Ag_2O .	8·0	> 14
$Pt(OH)_2$	~2·5	?	**$Cd(OH)_2$.	8·3	> 14
$Th(OH)_4$	3·0	> 14	$Mn(OH)_2$.	8·3	> 14
$Pd(OH)_2$	~3·5	?	$Mg(OH)_2$.	9·6–10·6	> 14
$In(OH)_3$	3·4	14			

*Notes.***—Basic salts can be precipitated before the hydroxide: BiOCl, SbOCl, etc. Formation of colloids can impede the separation of hydroxides by filtration: this is the case for the majority of hydroxides in the III, IV, and V state of oxidation.

The values given can be modified by the influence of temperature and other salts.

The solubility of the hydroxides varies with the size and perfection of the particles of the precipitate, sometimes within quite wide limits. We have indicated, wherever possible, the two limiting values.

The formation of complexes with Cl^-, SO_4^{2-} can retard the precipitation of hydroxide. We indicate here the theoretical (and not the apparent) pH's of precipitation, thus in general in perchloric acid solution.

Regions of predominance of hydroxides and of ions.—The regions of predominance of the different ions are delimited by the curve of solubility as a function of pH. The concentrations of M^+ and MO^- indicated at each pH cannot be exceeded.

SOLUBILITY OF SALTS AS A FUNCTION OF pH

Salts of strong acids.—The addition of nitric acid to silver chloride, the salt of a strong acid, only produces a small increase in its solubility due to an increase in the ionic strength of the solution.

Salts of weak acids.—Consider silver nitrite, $AgNO_2$. We have the equilibrium:

$$AgNO_2 \downarrow \rightleftharpoons Ag^+ + NO_2^- \quad . \quad . \quad . \quad . \quad \text{(I)}$$
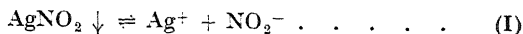
the NO_2^- ions are basic, and we have

$$HNO_2 \rightleftharpoons NO_2^- + H^+ \quad . \quad . \quad . \quad . \quad \text{(II)}$$

The addition of H^+ ions will displace equilibrium (II) to the left; the NO_2^- ions will disappear and as a result the equilibrium (I) will be displaced to the right, and some silver nitrite will dissociate. Thus, the net result is that addition of H ions causes silver nitrite to dissolve.

The relationships which govern this are as follows:

$$|NO_2^-|.|Ag^+| = s; \quad \frac{|NO_2^-|.|H^+|}{|HNO_2|} = K_A$$

the solubility $\quad S = |Ag^+| = |NO_2^-| + |HNO_2|$

Eliminating $|NO_2^-|$ and $|HNO_2|$, we find

$$S = |Ag^+| = \sqrt{s\left(1 + \frac{|H^+|}{K_A}\right)}$$

The solubility is the greater, the greater the solubility product, the greater $|H^+|$ and the smaller the acidity constant of the acid.

We get the solubility curve as shown in the diagram (fig. 21). The solubility varies rapidly when $|H^+| > K_A$ or when pH $< pK_A$.

The salts of weak acids have a solubility in acid solution which is the greater, the smaller the acidity constant K_A (or the larger pK_A).

However, if the initial solubility is extremely small, it can remain, in spite of everything that has been said, very small, even in very strongly acid solution.
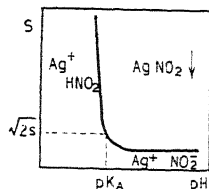
FIG. 21. — APPARENT SOLUBILITY OF SILVER NITRITE AS A FUNCTION OF pH

Solubility products of sulphides.—We give below some indications of solubility products for sulphides.

MnS	. . .	$10^{-15\cdot2}$	to	$10^{-22\cdot0}$	Bi_2S_3	. . .	$10^{-71\cdot8}$			
		(pink)		(green)	SnS	. . .	$10^{-28\cdot1}$			
FeS	. . .	$10^{-18\cdot4}$	,,	$10^{-21\cdot6}$	Fe_2S_3	. . .	10^{-88}			
Tl_2S	. . .	$10^{-22\cdot3}$	,,	$10^{-23\cdot9}$	Hg_2S	. . .	10^{-30}	to	10^{-45}
NiS	. . .	10^{-22}	,,	$10^{-27\cdot7}$	CuS	. . .	$10^{-44\cdot1}$			
CoS	. . .	$10^{-22\cdot2}$	,,	$10^{-26\cdot7}$	Ag_2S	. . .	$10^{-48\cdot1}$	to	$10^{-51\cdot2}$
ZnS	. . .	$10^{-22\cdot9}$	,,	$10^{-25\cdot2}$	Cu_2S	. . .	$10^{-49\cdot6}$			
CdS	. . .	$10^{-27\cdot2}$	,,	$10^{-28\cdot4}$	HgS	. . .	$10^{-52\cdot4}$	to	$10^{-53\cdot5}$
PbS	. . .	$10^{-27\cdot4}$	,,	10^{-29}	PtS	. .	$\sim 10^{-70}$			

Note.—The remarks already made about hydroxides can be repeated here (p. 72). The precipitation of sulphides is frequently accompanied by complicated phenomena and by the formation of colloids. The considerations developed here can only be regarded as first approximations, and they cannot be anything else.

To a first approximation, several solubility products can be used for the same sulphide according to the state of development of its precipitate; the extreme solubility products given in the above table permit one to predict at least on the one hand the precipitation point (greatest solubility) and on the other hand the redissolution point (precipitate developed to a stage corresponding to the smallest solubility).

Better approximations can be obtained from simple equilibria in solution. Thus it has been shown that in solution, along with Ag^+ there are considerable amounts of AgHS and AgS^-.

Below we shall develop some very simple considerations which give some qualitative indications.

Dissolution of sulphides as a function of pH.—Consider the sulphide MS. Its solubility product is

$$| M^{2+} | . | S^{2-} | = s$$

When the pH decreases, S^{2-} tends to disappear and to be replaced by HS^-, and then by H_2S.

$$S^{2-} + H^+ \rightleftharpoons HS^-, \qquad HS^- + H^+ \rightleftharpoons H_2S$$

$$\frac{| S^{2-} | . | H^+ |}{| HS^- |} = 10^{-15}$$

and

$$\frac{| HS^- | . | H^+ |}{| H_2S |} = 10^{-7}$$

whence

$$\frac{| S^{2-} | . | H^+ |^2}{| H_2S |} = 10^{-22}$$

The solubility of the sulphide MS can be measured by the activity of M^{2+} in solution. $S = | M^{2+} |$. Thus $| M^{2+} |$ is equal to

$$| S^{2-} | + | HS^- | + | H_2S |$$

since the quantities of M and S are initially equal in the sulphide MS.

Thus, similar to what we have seen for silver nitrite, we have

$$S = | M^{2+} | = | S^{2-} | + | HS^- | + | H_2S |$$
$$= | S^{2-} | \left[1 + \frac{| H^+ |}{10^{-15}} + \frac{| H^+ |^2}{10^{-22}} \right]$$

or
$$S^2 = |\,M^{2+}\,|.|\,S^{2-}\,| \left[1 + \frac{|\,H^+\,|}{10^{-15}} + \frac{|\,H^+\,|^2}{10^{-22}} \right]$$

whence
$$S = \sqrt{s}.\sqrt{1 + \frac{|\,H^+\,|}{10^{-15}} + \frac{|\,H^+\,|^2}{10^{-22}}}$$

whence we derive the solubility curve as a function of pH shown in fig. 22.

Below a pH of 7, the two first terms within the square root sign are negligible, so that the solubility varies as $\sqrt{s}\dfrac{|\,H^+\,|}{10^{-11}}$.

If $\sqrt{s}$ is very small, the solubility which varies rapidly below pH 7, by a factor of 10 for a variation of 1 unit of pH, can still remain very small. Thus, with mercury sulphide, we have $s = 10^{-52}$: at pH 0 we get $S = 10^{-15}$ which, for us, is still negligible. But in the case of ZnS we have $s = 10^{-25}$; thus for $|\,H^+\,| = 10^{-4\cdot5}$, i.e. at pH 4·5, the solubility is already 10^{-6} and at pH 1·5 it is 10^{-3}.

At pH 0 the soluble sulphides are those which satisfy the equation $\sqrt{s} \gg 10^{-13}$ or $s \gg 10^{-26}$.

Note.—The rate of dissolution of sulphides can be slow, sometimes even too slow for equilibrium to be attained in a reasonable time.

Another example.—We shall now treat the case of HgS which is a little more complicated. We have

FIG. 22.—APPARENT SOLUBILITY OF SULPHIDES AS A FUNCTION OF pH

$$|\,Hg^{2+}\,|.|\,S^{2-}\,| = 10^{-53}$$

and
$$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+; \qquad pK = 2\cdot8$$

The presence of other compounds such as $HgHS^+$ has still not been taken into account. Naturally we shall suppose that there are no complexes; thus in a hydrochloric solution there would be $HgCl^+$, $HgCl_2$, etc.

We thus have
$$Hg(II) \text{ total} = S(II^-) \text{ total}$$

since
$$|\,Hg^{2+}\,| + |\,HgOH^+\,| = |\,S^{2-}\,| + |\,HS^-\,| + |\,H_2S\,|$$

whence
$$|\,Hg^{2+}\,|\left[1 + \frac{10^{-2\cdot8}}{|\,H^+\,|} \right] = |\,S^{2-}\,|\left[1 + \frac{|\,H^+\,|}{10^{-15}} + \frac{|\,H^+\,|^2}{10^{-22}} \right]$$

Supposing that the solubility product is $|\,Hg^{2+}\,|\,|\,S^{2-}\,| = 10^{-53}$ we have

$$|\,Hg^{2+}\,| = \sqrt{10^{-53}\frac{1 + \dfrac{|\,H^+\,|}{10^{-15}} + \dfrac{|\,H^+\,|^2}{10^{-22}}}{1 + \dfrac{10^{-2\cdot8}}{|\,H^+\,|}}}$$

Precipitation of sulphides as a function of pH.—The conditions are somewhat different from those of the redissolution of precipitated sulphides. In effect, a large number of sulphides age after being brought down and their solubility sometimes varies quite considerably (NiS, CoS); the solubility product is thus occasionally larger in precipitation than in redissolution of a developed precipitate. On the other hand,

during precipitation, an excess of the reagent, either H_2S or ammonium sulphide, is always used.

A solution saturated with H_2S gives: $| H_2S | = 10^{-1}$ in acid solution of $pH \leqslant 6$.

Use of solubility curves.—*The salt is less soluble than the hydroxide.*— Fig. 23 presents the solubility curves for zinc sulphide and hydroxide. The sulphide is less soluble than the hydroxide: the precipitation pH's for 0·01M solutions are 1·4 for the sulphide and 6·8 for the hydroxide in acid solution.
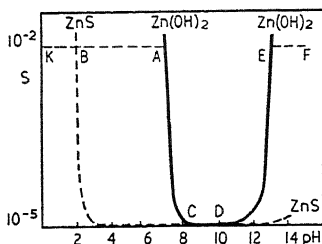
FIG. 23.—APPARENT SOLUBILITY OF ZINC SULPHIDE AND HYDROXIDE AS A FUNCTION OF pH

If we add caustic soda to a solution of a zinc salt at a pH of 0, the pH will increase along KA until the point is attained at which solubility product $| Zn^{2+} | . | OH^- |^2 = s$ is reached. Beyond this point, the addition of caustic soda precipitates the hydroxide and the pH does not vary much (AC) because the OH^- ions are used up in the reaction

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow$$
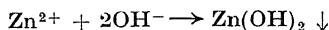
Later on the pH increases rapidly along CD until the point D is reached at which the hydroxide commences to redissolve:

$$Zn(OH)_2 \downarrow + OH^- \longrightarrow ZnO_2H^- + H_2O$$
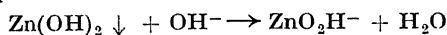
At E, the solution is clear.

Suppose now that, starting from the point K, we add sodium sulphide a little at a time to the solution, thus introducing S^{2-} into it. This is a fairly strong base, $pK = 15$:

$$2H^+ + S^{2-} \longrightarrow H_2S$$
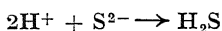
The pH will increase; when the solubility product of ZnS is reached, zinc sulphide is precipitated. If the addition of reagent is continued the S^{2-} ions will be used up until precipitation ceases. The pH will then rise rapidly.

The salt is more soluble than the hydroxide.—Example.—Precipitation of a zinc salt by sodium borate.

The relevant solubility products are

$$| Zn^{2+} | . | BO_2^- |^2 = s_1; \quad | Zn^{2+} | . | OH^- |^2 = s_2$$
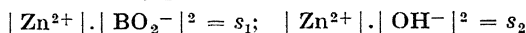
Suppose we have an acid solution of a zinc salt of concentration 0·01M, to which sodium borate is gradually added. The borate ion is a base

$$BO_2^- + H^+ \rightleftharpoons HBO_2$$
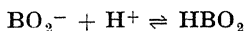
and the line KA on the graph (fig. 23) is followed. At the point A, zinc hydroxide commences to precipitate. If we have a sufficient excess of borate ions, s_1 can be exceeded and the precipitate will then be a mixture of zinc borate and hydroxide.

Generally, where the hydroxide is the less soluble compound, the addition of a salt of a weak acid will cause the hydroxide to be precipitated.

Another example.—Precipitation of aluminium salts by sodium sulphide.

If sodium sulphide is added to a solution of an aluminium salt, the basic S^{2-} ions will increase the pH this time until the solubility product of the hydroxide is reached, and $Al(OH)_3$ will be precipitated. Commencing at pH 10, the hydroxide will redissolve, and, with an excess of sodium sulphide, a solution of AlO_2^- is obtained.

$$Al^{3+} + 3H_2O + 3S^{2-} \longrightarrow Al(OH)_3 \downarrow + 3HS^-$$

$$Al(OH)_3 \downarrow + S^{2-} \longrightarrow AlO_2^-, H_2O + HS^-$$
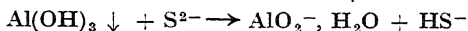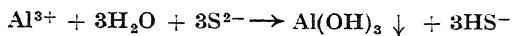
In the same way, the addition of sodium carbonate gives rise to the reactions

$$2Al^{3+}, 3H_2O + 3CO_3^{2-} \rightleftharpoons 2Al(OH)_3 \downarrow + 3CO_2 + 3H_2O$$
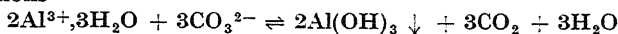
INFLUENCE OF PRECIPITATION ON pH

Inversely, precipitation can induce variations in the pH of the solution. Hydrocyanic acid, HCN, is a weak acid, $pK = 9 \cdot 2$. A normal solution of the acid has a pH of $4 \cdot 6$, and in this solution

$$|\, HCN\, | = 1; \quad |\, CN^-\, | = |\, H^+\, | = 10^{-4 \cdot 6}$$

Addition of Ag ions in excess will precipitate the slightly soluble AgCN:

$$Ag^+ + CN^- \longrightarrow AgCN \downarrow \quad \text{with} \quad |\, Ag^+\, | . |\, CN^-\, | = 10^{-14}$$
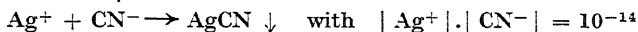
The CN^- ions will disappear and the equilibrium $HCN \rightleftharpoons H^+ + CN^-$ will be displaced towards the right: the acid dissociates, liberating CN^- and H^+ at the same time. The concentration of CN^- must remain small, because the solubility product of AgCN is small. It can be said that practically as many CN^- ions disappear as Ag ions can be supplied to partner them. If as many Ag ions as HCN are supplied, i.e. 1 equivalent, the H ion concentration will be equal to 1 and the pH will fall from $4 \cdot 6$ to 0.

HCN thus behaves like a strong acid.

The disappearance of one of the ions, acid or basic, by precipitation, apparently reinforces the acid or basic properties of the corresponding acid or base.

Experiment.—Take a solution of potassium dichromate of about $0 \cdot 01M$. Add to it a drop of bromocresol green:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$$
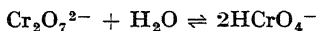
The bromocresol green is still green (yellow pH $3 \cdot 8$–pH $5 \cdot 4$ blue). Add some lead nitrate, which is neutral. The solution becomes acid, and the bromocresol green turns yellow:

$$HCrO_4^- + Pb^{2+} \longrightarrow PbCrO_4 \downarrow + H^+$$

7
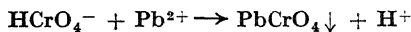
Buffering effect of hydroxides and of slightly soluble salts of weak acids.—Refer again to the solubility curve for aluminium hydroxide (fig. 20, p. 77). Suppose that we find ourselves at pH 8 with a precipitation of aluminium hydroxide. If we add H^+ ions the pH will decrease rapidly, down to pH 5. Below 5, the hydroxide will redissolve, using up H ions:

$$Al(OH)_3 \downarrow + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$
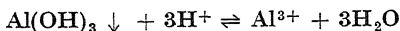
While the hydroxide is redissolving, the pH only varies slightly (vertical part of the solubility curve). The solution is buffered around a pH of 4–5; the pH is determined by the final concentration of aluminium ions in the solution. The same result may be obtained by adding aluminium hydroxide to an acid solution until it is present in excess, and in this way the pH is adjusted to have a value close to 4.

The pH of an alkaline solution can also be buffered (right branch of the solubility curve). Aluminium hydroxide added to an alkaline solution adjusts its pH to a value close to 11.

The same phenomena occur with the slightly soluble salts of weak acids or weak bases. This property can be applied in both qualitative and quantitative analysis.

PRECIPITATIONS IN SOLUTION OF CONTROLLED pH.— CLASSICAL METHOD OF QUALITATIVE ANALYSIS

The classical method of qualitative analysis involves the separation of the mixture into various groups by precipitation of the sulphides in a solution of fixed pH.

Sulphides only slightly soluble in 0·3–0·5N-HCl

A certain number of sulphides are precipitated by passing H_2S into a solution of controlled acidity. These sulphides are:

(1) Those of the *hydrogen sulphide group*: As(III), As(V), Sb(III), Sb(V), Sn(II) and Sn(IV).

Hg(II), Pb(II), Bi(III), Cu(II), Cd(II), Ag(I), Hg(I) would be precipitated under the same conditions.

(2) The *ammonium sulphide group*: The solution is brought to pH 9 by the addition of a mixture of NH_3 and NH_4^+ and ammonium sulphide is added. Those elements whose sulphides are soluble in acid solution but only slightly soluble in solution of pH 9 precipitate under these conditions: Ni(II), Co(II), Zn(II), Mn(II), Fe(II); Fe(III) is reduced and FeS precipitates.

The *ammonia group*: at the same time the elements whose hydroxides are only slightly soluble at this pH and whose sulphides are soluble precipitate: these are: Be(II), Al(III), Cr(III), rare earths (III), Ti(IV), Zr(IV), Th(IV), Nb(V), Ta(V).

(3) The elements whose sulphides and hydroxides are both soluble remain in solution. These are the alkaline earths and the alkalis.

A certain number of separations in controlled pH solution, mainly of use in quantitative analysis, can be carried out on the solution.

Separation with barium carbonate.—Formerly, the hydroxides $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ were separated from Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+},

by adding an excess of barium carbonate which remained for about 12 hours in contact with the solution. The method, which is frequently quantitative, entails the inconvenience of introducing barium into the solution.

Consider the solubility curves for the different hydroxides and the solubility curve for barium carbonate (fig. 24). The final pH of the solution is determined by the concentration of barium which passes into solution. It is in general about 5–6. The desired separation can therefore be achieved.
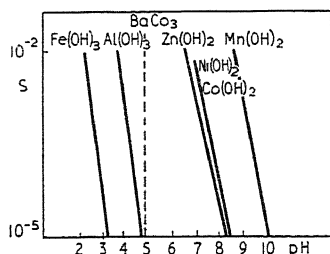
FIG. 24.—APPARENT SOLUBILITY OF SOME HYDROXIDES AS A FUNCTION OF pH
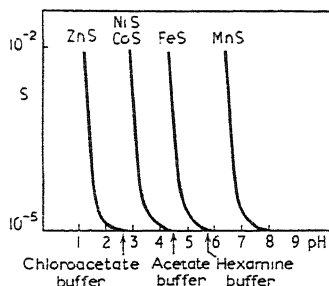
FIG. 25.—APPARENT SOLUBILITY OF SOME SULPHIDES AS A FUNCTION OF pH

Separation of sulphides (fig. 25).—(*a*) In a solution buffered with chloroacetic acid–sodium chloroacetate mixture, pH 2·5, only zinc sulphide precipitates.

(*b*) In acetate buffered solution, pH 4·5, the sulphides of zinc, nickel, and cobalt precipitate quantitatively, and ferrous sulphide comes down partially.

(*c*) When the solution is buffered at 5·4 by hexamethylenetetramine-hexamethylenetetramine hydrochloride, the sulphides of zinc, nickel, cobalt and iron precipitate quantitatively, while that of manganese remains in solution.

Separation of phosphate ions.—These ions interfere when the alkaline earths are being sought. Both in the new and the classical method, alkaline earths are looked for after the other ions have been separated from the solution. This is obtained by precipitation of the sulphides at pH 9 resulting from the addition of $NH_3 + NH_4^+$. Under these conditions, the presence of phosphate ions brings about the precipitation of the phosphates of the alkaline earths, which are of low solubility in alkaline solution, at the same time as the sulphides.

This inconvenience is avoided by the preliminary precipitation of a low-solubility phosphate in acid solution: the alkaline earths then remain dissolved. The principal methods proposed use either ferric phosphate in acetate buffer, or zirconium phosphate in very dilute acid, or the phosphates of lead and bismuth in acetic acid solution.

Thus either Fe(III), Zr(IV), Bi(III), or Pb(II) are added to the solution in excess, and the precipitation is carried out by adjusting the pH

accordingly. In the case of Fe(III) and Zr(IV), the excess of the metal precipitates as the hydroxide at the same time as the phosphate.

The separation as lead phosphate is described on page 151.

After this, separations can be made in solutions which have been cleared of phosphate ions, by rendering them ammoniacal. The alkaline earths then remain in solution.

Separation by caustic soda.—In strongly alkaline solution, N–2N-NaOH, a certain number of elements remain in solution. These are the alkalis, Ca^{2+}, Ba^{2+}, Sr^{2+}, BeO_2^-, AlO_2^-, CrO_2^-, GaO_2^-. Prolonged boiling, particularly in alkaline solution, precipitates $Cr(OH)_3$ completely, then $Be(OH)_2$ partially, and finally $Al(OH)_3$ with difficulty; ZnO_2^{2-}; $Cu(OH)_2$ slowly redissolves to give a blue solution in strongly alkaline solution; dilution and boiling reprecipitates it; PbO_2^-, PbO_3^{2-}, AsO_2^-, SbO_2^-, SbO_3^-, SnO_3^-, MnO_4^{2-}, WO_4^{2-}, VO_3^-.

Method for the separation of the elements soluble in alkaline solution.—The hydroxides of low solubility which precipitate during this separation unfortunately occlude a number of these ions if precautions are not taken. The best conditions are as follows:

Neutralize the solution with N–2N caustic soda until precipitation just commences. Bring to the boil. Boil up a volume of 2N–NaOH equal to $1\frac{1}{2}$ times the volume of the solution which has been neutralized. Run the boiling neutralized solution drop by drop into the boiling NaOH solution, agitating at the same time. Filter after a few minutes.

CHAPTER XII

PRECIPITATION AND COMPLEXES

Formation of a precipitate.—The complex produced from Ag ions and ammonia, $Ag(NH_3)_2{}^+$, is slightly ionized:

$$Ag(NH_3)_2{}^+ \rightleftharpoons Ag^+ + 2NH_3$$
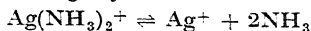
Its stability is determined by the relationship:

$$\frac{|\ Ag^+\ |.|\ NH_3\ |^2}{|\ Ag(NH_3)_2{}^+\ |} = K = 10^{-7} \quad . \quad . \quad . \quad . \quad (I)$$

Suppose that the total silver concentration is 10^{-2}. The complex is only slightly dissociated, we have $|\ Ag(NH_3)_2{}^+\ | \sim 10^{-2}$.

The concentration of free Ag ions is given by: $|\ Ag^+\ |.|\ NH_3\ |^2 \sim 10^{-9}$; thus $2\ |\ Ag^+\ | = |\ NH_3\ |$ whence $|\ Ag^+\ | = 10^{-3.2}$.

Suppose that chloride ions are added to the solution of the complex. The low-solubility silver chloride has a solubility product of

$$|\ Ag^+\ |.|\ Cl^-\ | = 10^{-9.7}$$

As soon as the activity of the chloride ions reaches such a figure that the s.p. of the silver chloride is exceeded, this compound will precipitate. As $|\ Ag^+\ | = 10^{-3.2}$ precipitation will commence when

$$|\ Cl^-\ | = \frac{10^{-9.7}}{10^{-3.2}} = 10^{-6.5}$$

that is to say almost immediately after the addition of chloride ions commences. Under these conditions, the silver ion is not sequestered from reaction with the chloride ion.

Suppose now that there is an excess of ammonia; according to (1) the concentration of Ag ions will diminish, and the complex becomes stabilized. For example if $|\ NH_3\ | = 1$, $|\ Ag(NH_3)_2{}^+\ |$ is always fairly near to 10^{-2}M and $|\ Ag^+\ | = 10^{-7}/100 = 10^{-9}$. Silver chloride will precipitate for $|\ Cl^-\ | = 10^{-9.7}/10^{-9} = 10^{-0.7}$M, thus at a chloride ion concentration of about 0·2M.

The formation of a precipitate when a reagent is added to a complex depends upon the stability of the complex and the solubility of the precipitate.

Dissolution of a precipitate due to the formation of a complex.—Inversely, if ammonia is gradually added to a precipitate of silver chloride, the precipitate will redissolve due to the formation of the complex ion $Ag(NH_3)_2{}^+$. Supposing that the precipitate completely redissolves to a concentration of 10^{-2}M, which is the concentration most frequently met with in analysis, the following relations will apply.

$$|\ Ag^+\ |.|\ Cl^-\ | = 10^{-9.7} \quad \text{with} \quad |\ Cl^-\ | = 10^{-2}$$

$$\frac{|\ Ag^+\ |.|\ NH_3\ |^2}{|\ Ag(NH_3)_2{}^+\ |} = 10^{-7} \quad \text{with} \quad |\ Ag(NH_3)_2{}^+\ | = 10^{-2}$$

whence $|\ Ag^+\ | = 10^{-7.7}$ and $|\ NH_3\ |^2 = 10^{-1.3}$; $|\ NH_3\ | = 0.25$

Dissolution will thus be complete in 0·3N ammonia.

In the case of silver bromide, the precipitate is less soluble:

$$|\,Br^-\,|\,.\,|\,Ag^+\,| \;=\; 10^{-12\cdot3}$$
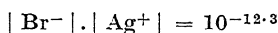
Redissolution, which requires the $|\,NH_3\,|$ to be 3N, can only be partial in N-NH_3. Silver iodide, much less soluble, only dissolves a little, even in concentrated ammonia. $|\,I^-\,|$ would be $10^{-3\cdot5}$ for $|\,NH_3\,| \;=\; 10$.

Low-solubility complex compounds.—Complex ions themselves can yield low-solubility compounds.

$$Ag(CN)_2{}^- \;+\; Ag^+ \;\rightleftharpoons\; Ag[Ag(CN)_2] \downarrow$$

$$Co(CN)_6{}^{3-} \;+\; 3Ag^+ \;\rightleftharpoons\; Ag_3[Co(CN)_6] \downarrow, \text{ etc.}$$
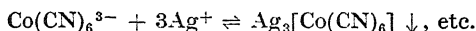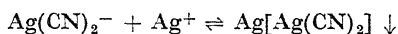
Disproportionation.—Precipitation displaces disproportionation equilibria. Thus in the series of complex aluminium fluorides, AlF^{2+}, $AlF_2{}^+$, AlF_3, $AlF_4{}^-$, $AlF_5{}^{2-}$, $AlF_6{}^{3-}$, there are two low-solubility compounds Na_3AlF_6 and AlF_3 (more exactly $Al(AlF_6)$); the neighbouring complexes are disproportionated, for example:

$$2AlF_2{}^+ \;\rightleftharpoons\; AlF^{2+} \;+\; AlF_3 \downarrow$$

so that $AlF_2{}^+$, $AlF_4{}^-$, $AlF_5{}^{2-}$ scarcely exist.

Influence of pH.—Complexes can be destroyed by variations of pH, as we have already seen on page 47. This destruction can be promoted by the formation of low-solubility compounds.

$$Ag(CN)_2{}^- \;\rightleftharpoons\; AgCN \downarrow \;+\; CN^-$$
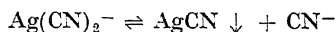
Addition of acid displaces the equilibrium to the right:

$$Ag(CN)_2{}^- \;+\; H^+ \;\rightleftharpoons\; AgCN \downarrow \;+\; CN^-$$
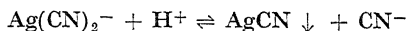
The complex $Ag(CN)_2{}^-$ is destroyed by the addition of acid with precipitation of AgCN (in reality $Ag[Ag(CN)_2]$).

Precipitation of hydroxides in complexes.—Consider the ferri-fluoride complex FeF^{2+}. Since $Fe(OH)_3$ is of low solubility, when the concentration of OH^- ions increases, the s.p. $|\,Fe^{3+}\,|\,.\,|\,OH^-\,|^3 = s$ can easily be exceeded and ferric hydroxide will precipitate. This is a particular case of the precipitation already seen.

The precipitation pH of the hydroxide indicates the stability of the complex.—Take the case of ferric ions. We have

$$|\,Fe^{3+}\,|\,.\,|\,OH^-\,|^3 \;=\; s$$
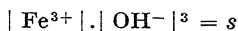
or
$$pFe^{3+} \;+\; 3pOH^- \;=\; -\log s$$

or again
$$pFe^{3+} \;+\; 42 \;-\; 3p\mathrm{H} \;=\; -\log s$$

or
$$p\mathrm{H} \;=\; \frac{pFe^{3+} \;+\; 42 \;+\; \log s}{3} \;=\; \frac{pFe^{3+}}{3} \;+\; (\text{const.})$$

The precipitation pH of ferric hydroxide is directly related to the concentration of free Fe^{3+} ions, and thus to the stability of the complex. The larger $|\,Fe^{3+}\,|$ is, the lower the precipitation pH will be. Thus, for 0·1M solution with a ten-fold excess of the complex-forming ion, we have

$ClO_4{}^-$, $NO_3{}^-$	.	pH 1·8 (no complex)		$C_2O_4{}^{2-}$	.	.	.	.	pH 7·7
Cl^- .	. .	pH 2·0		$Fe(CN)_6{}^{3-}$ does not precipi-					
$SO_4{}^{2-}$	. . .	pH 2·5		tate, even at .	.	.	.	.	pH 14
CNS^-	. . .	pH 2·7							

Various examples.—(1) If iodide is added to a mercuric salt Hg^{2+} there will be at first a precipitation of the red mercuric iodide

$$Hg^{2+} + 2I^- \rightleftharpoons HgI_2 \downarrow \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$

An excess of iodide redissolves the precipitate.

$$HgI_2 \downarrow + 2I^- \rightleftharpoons HgI_4^{2-}$$
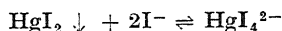
The addition of the mercuric salt to the complex will naturally reprecipitate the iodide:

$$HgI_4^{2-} + Hg^{2+} \rightleftharpoons 2HgI_2 \downarrow$$
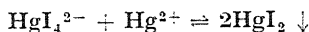
The addition of an ion capable of withdrawing I^- ions by precipitation will destroy the complex by displacing the equilibrium (I) to the left:

$$2Ag^+ + HgI_4^{2-} \rightleftharpoons 2AgI \downarrow + HgI_2 \downarrow$$
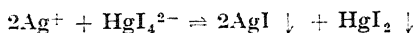
(2) The low-solubility fluorides, CaF_2, Na_3AlF_6, are dissolved by compounds which cause F^- to disappear by the formation of complexes, for example Al(III), Zr(IV), B(III), Sn(IV), etc. Excess of these ions diminishes the concentration of F^-, and thus favours the dissolution. We have

$$CaF_2 \downarrow \rightleftharpoons Ca^{2+} + 2F^-$$

and

$$F^- + Al^{3+} \rightleftharpoons AlF^{2+}$$
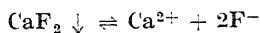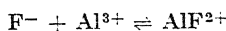
whence the reaction in the presence of aluminium ions is

$$CaF_2 \downarrow + 2Al^{3+} \longrightarrow Ca^{2+} + 2AlF^{2+}$$

similarly

$$Na_3AlF_6 \downarrow \rightleftharpoons AlF_6^{3-} + 3Na^+$$

with

$$AlF_6^{3-} \rightleftharpoons Al^{3+} + 6F^-$$

$$F^- + Al^{3+} \longrightarrow AlF^{2+}$$

whence the reaction

$$Na_3AlF_6 \downarrow + 5Al^{3+} \longrightarrow 3Na^+ + 6AlF^{2+}$$
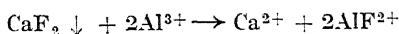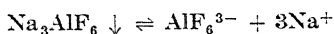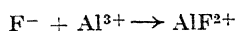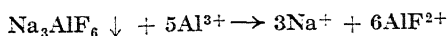
(3) Lead sulphate has a moderately low solubility. It can be redissolved by the addition of a large excess of acetate ions, yielding acetate complexes with the Pb(II). The lead can be reprecipitated; e.g. by the addition of an acid which destroys the acetate complex:

$$CH_2CO_2^- + H^+ \longrightarrow CH_3CO_2H$$
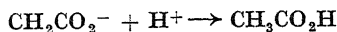
and, better still, by sulphuric acid which, at the same time, decreases the concentration of Pb^{2+} in solution:

$$SO_4^{2-} + Pb^{2+} \longrightarrow PbSO_4 \downarrow$$
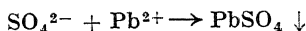
and by precipitation of the very low-solubility compounds $PbCrO_4$ or PbS.

(4) Fe^{3+}, Cr^{3+}, etc., impede the precipitation of calcium oxalate by the formation of oxalate complexes.

(5) F^- ions inhibit the precipitation of SnS_2 by the formation of stannifluoride complexes. If compounds which decrease the activity of F^- ions are added, the precipitation of SnS_2 should be promoted. This happens with boric acid.

APPLICATIONS

Detection of phosphate and arsenate ions.—Phosphate and arsenate ions give yellow precipitates with molybdate (Mo(VI)) reagent, these precipitates being ammonium phosphomolybdate of very low solubility and ammonium arsenimolybdate of somewhat higher solubility:

$$| \ PO_4{}^{3-} \ |^m.| \ MoO_4{}^{2-} \ |^n \ldots = s_1 \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \qquad (I)$$

$$| \ AsO_4{}^{3-} \ |^m.| \ MoO_4{}^{2-} \ |^n \ldots = s_2; \quad s_2 > s_1 \quad \cdot \quad \cdot \qquad (II)$$
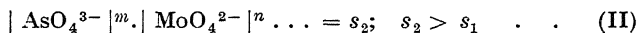
The sensitivity of the reaction (I) is thus greater than that of (II), i.e. at the same concentration of $MoO_4{}^{2-}$ ions smaller quantities of $PO_4{}^{3-}$ than of $AsO_4{}^{3-}$ can be detected.

Tartrate ions form complexes with molybdate ions, that is to say they diminish the sensitivity of the reaction. They also form complexes with As(V) and not with P(V). At a suitable concentration of tartrate ions, the molybdate ions do not react with As(V), but still do so with P(V).

To detect phosphates and arsenates, the procedure should be to start with the reaction with molybdate reagent in the presence of tartrate ions, the reaction is then specific for phosphate ions. If the reaction is negative, the arsenate ion can then be sought for with the molybdate reagent. If the reaction for phosphate ions is positive, they must be separated before going on to look for arsenates, or As(V) can be detected by another method (see p. 224).

Detection of cadmium (p. 203).—Cd^{2+} can scarcely be detected by the yellow colour of its sulphide, for there are several black sulphides which mask the yellow colour of CdS, and they must be separated. This can be achieved by the formation of a complex. A preliminary separation with ammonia leaves in solution only the ammine complexes of the following metals: Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}, etc.

The subsequent addition of cyanide gives the low-stability cyanide complexes of Zn^{2+} and Cd^{2+}, the more stable ones of Ni^{2+}, and the very stable ones of Co^{3+} and Cu^+. The addition of sulphide now precipitates only ZnS and CdS. At the same time, if the concentration of CN^- is too low, black NiS will precipitate. Thus, if a black precipitate forms, the precipitation of sulphide is repeated in a separate part of the solution, to which a little more cyanide has been added. The detection of Cd^{2+} is evidently less sensitive in the presence of CN^- on account of the formation of $Cd(CN)_4{}^{2-}$.

Detection of potassium.—Sodium cobaltinitrite $Na_3Co(NO_2)_6$ gives with K ions a yellow precipitate:

$$Co(NO_2)_6{}^{3-} + Na^+ + 2K^+ \rightleftharpoons K_2NaCo(NO_2)_6 \downarrow$$
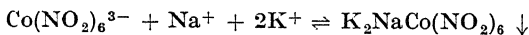
Excess of reagent.—Excess of either reagent, Na^+ or $Co(NO_2)_6{}^{3-}$ ions, displaces the equilibrium to the right and thus renders the reaction more sensitive.

Influence of pH.—$Co(NO_2)_6{}^{3-}$ behaves as a very weak base conjugate with a strong complex acid, thus the pH should be without influence: at the same time, there is the equilibrium

$$Co(NO_2)_6{}^{3-} \rightleftharpoons Co^{3+} + 6NO_2{}^-$$
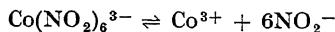
Co^{3+} is a strong acid which cannot exist in other than very low concentration in water because

$$Co^{3+},3H_2O \rightleftharpoons Co(OH)_3 \downarrow + 3H^+$$
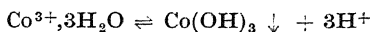
Thus, in sufficiently alkaline solution, $Co(OH)_3$ precipitates, the complex ion is destroyed and the potassium compound is not precipitated. NO_2^- is a base, $pK = 3.4$, thus, in sufficiently acid solution, the complex is destroyed by the formation of HNO_2. The reaction must thus be carried out in a solution that is neither too acid nor too alkaline. Experience shows that an acetate buffer is suitable.

Interfering substances.—(1) *Oxidants and reductants.*—It will be seen that ions which are too strongly oxidizing or reducing will interfere by destroying the complex.

(2) *Complexes.*—Similarly ions which form complexes more strongly with Co^{3+} than NO_2^- ions, such as CN^-, will interfere.

(3) *Precipitating ions.*—Those which can form precipitates interfere. There are no ions which precipitate NO_2^- or Co^{3+}. Ammonium ions can precipitate $Co(NO_2)_6^{3-}$, just as can a great number of other cations, which must be separated before carrying out the reaction.

CHAPTER XIII

PRECIPITATION AND REDOX*

I. REDOX PROPERTIES OF THE ELEMENTS

THE majority of the elements are of low solubility, and their formation by oxidation or reduction involves their precipitation.

In the system $Ag^+ + e \rightleftharpoons Ag \downarrow$ the redox potential is given by

$$E = E_0 + 0.06 \log \frac{|Ag^+|}{|Ag|}$$

The activity of Ag in the solid is constant (taken $= 1$ by convention) and so we get

$$E = 0.80 + 0.06 \log |Ag^+| \text{ volt}$$

In this way a potential of a new kind is defined. The value of this potential when $|Ag^+| = 1$, i.e. 0.80 volt here, is called the normal or standard potential.

Similarly we have

$$S^{2-} - 2e \rightleftharpoons S \downarrow$$
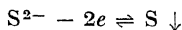
with

$$E = 0.51 - 0.03 \log |S^{2-}| \text{ volt}$$

Disproportionation.—In the redox systems,

$$Cu^{2+} + e \rightleftharpoons Cu^+ \quad E_0 = 0.17 \text{ volt}$$

and

$$Cu^+ + e \rightleftharpoons Cu \downarrow \quad E'_0 = 0.52 \text{ volt}$$
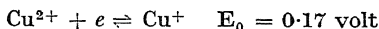
As a result of the precipitation of copper, the oxidizing properties of Cu^+ are reinforced and E'_0, which is the formal normal potential, becomes larger than E_0. The second system oxidizes the first, in other words Cu^+ reacts with itself

$$Cu^+ + Cu^+ \rightleftharpoons Cu \downarrow + Cu^{2+}$$
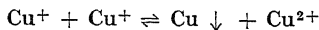
This is equivalent to saying that the disproportionation equilibrium is displaced to the right as a result of the precipitation of copper. At equilibrium we have

$$E = 0.17 + 0.06 \log \frac{|Cu^{2+}|}{|Cu^+|} = 0.52 + 0.06 \log |Cu^+| \text{ volt}$$

whence

$$\log \frac{|Cu^{2+}|}{|Cu^+|^2} = 6 \quad \text{or} \quad \frac{|Cu^{2+}|}{|Cu^+|^2} = 10^6$$

Cu^+ introduced into the solution disappears and is replaced by Cu^{2+} and $Cu \downarrow$ until the concentrations are in agreement with the latter relationship. The cuprous ions are therefore more or less non-existent in solution, and the only redox system of interest is

$$Cu^{2+} + 2e \longrightarrow Cu \downarrow \quad \text{with} \quad E = 0.35 + 0.03 \log |Cu^{2+}| \text{ volt}$$
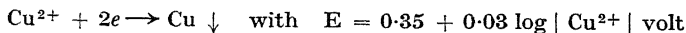
* In the rest of this book, 'redox' will be used instead of 'oxidation-reduction'.

Normal redox potentials of metals

	Volts		Volts
$Li^+ + e \rightleftharpoons Li \downarrow$	$-3 \cdot 02$	$Tl^+ + e \rightleftharpoons Tl \downarrow$	$-0 \cdot 34$
$Sr^{2+} + 2e \rightleftharpoons Sr \downarrow$	$-2 \cdot 95$	$Co^{2+} + 2e \rightleftharpoons Co \downarrow$	$-0 \cdot 28$
$K^+ + e \rightleftharpoons K \downarrow$	$-2 \cdot 92$	$Ni^{2+} + 2e \rightleftharpoons Ni \downarrow$	$-0 \cdot 24$
$Ba^{2+} + 2e \rightleftharpoons Ba \downarrow$	$-2 \cdot 9$	$Sn^{2+} + 2e \rightleftharpoons Sn \downarrow$	$-0 \cdot 14$
		$Pb^{2+} + 2e \rightleftharpoons Pb \downarrow$	$-0 \cdot 13$
$Ca^{2+} + 2e \rightleftharpoons Ca \downarrow$	$\sim -2 \cdot 8$	$2H^+ + 2e \rightleftharpoons H_2 \uparrow$	$0 \cdot 00$
$Na^+ + e \rightleftharpoons Na \downarrow$	$-2 \cdot 71$	$Sb^{3+} + 3e \rightleftharpoons Sb \downarrow$	$+0 \cdot 10$
$Mg^{2+} + 2e \rightleftharpoons Mg \downarrow$	$\sim -2 \cdot 4$	$Bi^{3+} + 3e \rightleftharpoons Bi \downarrow$	$+0 \cdot 23$
$Be^{2+} + 2e \rightleftharpoons Be \downarrow$	$-1 \cdot 78$	$As^{3+} + 3e \rightleftharpoons As \downarrow$	$+0 \cdot 3$
$Ce^{3+} + 3e \rightleftharpoons Ce \downarrow$	$-1 \cdot 68$	$Cu^{2+} + 2e \rightleftharpoons Cu \downarrow$	$+0 \cdot 345$
$Al^{3+} + 3e \rightleftharpoons Al \downarrow$	$-1 \cdot 67$	$Ag^+ + e \rightleftharpoons Ag \downarrow$	$+0 \cdot 80$
$Mn^{2+} + 2e \rightleftharpoons Mn \downarrow$	$-1 \cdot 05$	$Hg_2^{2+} + 2e \rightleftharpoons 2Hg \downarrow$	$+0 \cdot 80$
$Zn^{2+} + 2e \rightleftharpoons Zn \downarrow$	$-0 \cdot 76$	$Pd^{2+} + 2e \rightleftharpoons Pd \downarrow$	$\sim +0 \cdot 99$
$Cr^{2+} + 2e \rightleftharpoons Cr \downarrow$	$-0 \cdot 56$	$Pt^{2+} + 2e \rightleftharpoons Pt \downarrow$	$\sim +1 \cdot 2$
$Fe^{2+} + 2e \rightleftharpoons Fe \downarrow$	$-0 \cdot 44$	$Au^+ + e \rightleftharpoons Au \downarrow$	$+1 \cdot 46$
$Cd^{2+} + 2e \rightleftharpoons Cd \downarrow$	$-0 \cdot 40$		

Normal redox potentials of non-metals

	Volt		Volts
$Te^{2-} - 2e \rightleftharpoons Te \downarrow$	$-0 \cdot 92$	$I_2 + 2e \rightleftharpoons 2I^-$	$+0 \cdot 62$
$Se^{2-} - 2e \rightleftharpoons Se \downarrow$	$-0 \cdot 77$	$Br_2 + 2e \rightleftharpoons 2Br^-$	$+1 \cdot 09$
$S^{2-} - 2e \rightleftharpoons S \downarrow$	$-0 \cdot 51$	$Cl_2 + 2e \rightleftharpoons 2Cl^-$	$+1 \cdot 41$
$AsH_3 \uparrow - 3e \rightleftharpoons As \downarrow + 3H^+$	$-0 \cdot 54$	$F_2 + 2e \rightleftharpoons 2F^-$	$+2 \cdot 85$
$SbH_3 \uparrow - 3e \rightleftharpoons Sb \downarrow + 3H^+$	$-0 \cdot 5$		(calc.)

Attack on a metal

Chemical attack on a metal transforms it from a zero to a positive state of oxidation, and is thus an oxidation. Consideration of redox potentials gives valuable information.

Attack by acids.—The two redox systems involved are

$$Me^{n+} + ne \rightleftharpoons Me \downarrow \quad \ldots \quad \ldots \quad (I)$$

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow \quad \ldots \quad \ldots \quad (II)$$
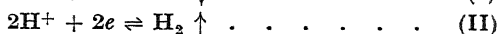
with the potentials:

$$E = E_0 + \frac{0 \cdot 06}{n} \log |Me^{n+}| \quad \ldots \quad \ldots \quad (I)$$

$$E' = -0 \cdot 06 \, pH \text{ for unit } H_2 \text{ pressure} \quad \ldots \quad (II)$$

Take the case of aluminium for example. When this metal is put in contact with water, the following two redox systems are obtained:

$$Al^{3+} + 3e \rightleftharpoons Al \downarrow \quad \ldots \quad \ldots \quad (I)$$

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow \quad \ldots \quad \ldots \quad (II)$$

and
$$E = -1 \cdot 6 + 0 \cdot 02 \log |Al^{3+}| \text{ volts}$$

for which

$$E' = -0 \cdot 06 \, pH - 0 \cdot 03 \log pH_2; \quad pH_2 \text{ being the pressure of the } H_2$$

In N acid solution, $pH = 0$, system (II) can oxidize system (I) and we get the following equation for the attack of acids on aluminium:

$$\text{Al} \downarrow + 3\text{H}^+ \longrightarrow \text{Al}^{3+} + \tfrac{3}{2}\text{H}_2 \uparrow$$
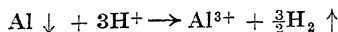
The more reducing the metal, the more easily it is attacked by acids. The alkali metals reduce the hydrogen ions of water, even in alkaline solution:

$$\text{Na} \downarrow + \text{H}^+ \longrightarrow \text{Na}^+ + \tfrac{1}{2}\text{H}_2 \uparrow$$
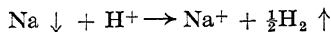
Thus the attack of acids on metals can be predicted. The potentials are given on page 93.

Oxidizing attack.—In addition to the oxidizing action of its hydrogen ions, nitric acid can act as a more powerful oxidizing agent in the system

$$\text{NO}_3^- + 4\text{H}^+ + 3e \longrightarrow \text{NO} \uparrow + 2\text{H}_2\text{O} \quad \text{E}_0 = 0.95 \text{ volt at } pH = 0$$
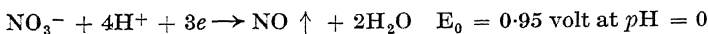
Sulphuric acid can act as an oxidant if it is concentrated and hot. The same applies to perchloric acid at its b.p.

Similar sort of attack can be obtained by the oxidizing mixtures $\text{HCl} + \text{Br}_2$, $\text{HCl} + \text{ClO}_3^-$, etc.

Overvoltage.—In practice, phenomena are more complicated. The reduction of H^+ ions does not occur at any reasonable speed until the potential is in general lower than that predicted. This difference between the potential calculated and that actually observed is called the 'overvoltage' or 'over-potential' (see p. 108). There are other causes of disturbance as well, such as:

(*a*) *Passivation*—the metal becomes coated with a protective film of oxide, for example, and the attack ceases. Examples are V, W, Mo, Cr, U.

(*b*) *Impurities* can exert an effect on the rate of attack. Thus very pure aluminium is only attacked very slowly.

(*c*) The *physical state of the metal.*—Finely divided metals present a large surface for attack and the rate of attack is then greater, and can become very high indeed.

Reduction by metals

Reduction by metals and amalgams is much used in quantitative, and it has a limited applicability in qualitative, analysis.

Reduction in acid solution.—Reduction by copper.—A drop of solution is placed on a piece of sheet copper. It can be seen from the table of normal potentials that copper precipitates the following metals: gold (1·46 volts), platinum (1·2 volts), silver (0·80 volt), mercury (0·80 volt). Gold and platinum are not often met with, and silver is not present in a hydrochloric acid solution: the test is used in looking for mercury (p. 220).

Reduction by tin.—Tin reduces numerous ions to the metallic state in HCl solution. Besides the preceding metals, antimony and bismuth are rapidly precipitated (black stain), arsenic slowly (brown stain) and copper very slowly, in hydrochloric acid solution.

Antimony and bismuth can thus be detected (p. 217). Reduction is obtained by depositing a drop of the solution on a piece of tin foil. Hg (II) is previously separated (and driven off) by heating with copper powder which produces Hg.

Reduction in alkaline solution.—In 2N-NaOH the following systems can be used:

Oxidant	Reductant	
$Ag_2O \downarrow \longrightarrow Ag \downarrow$ 0·30 volt		
$HgO \downarrow \longrightarrow Hg \downarrow$ 0·10 ,,		
$Bi(III) \longrightarrow Bi \downarrow$ $- 0·40$,,		
	$Sb(III) \longrightarrow Sb(V)$ $- 0·5$–$0·6$ volt	more
$As(III) \longrightarrow As \downarrow$		reducing
$Sb(III) \longrightarrow Sb \downarrow$ $- 0·5$–$0·6$ volt		
	$Fe(II) \longrightarrow Fe(III)$ $- 0·7$ volt	
	$Sn(II) \longrightarrow Sn(IV)$ $- 0·9$,,	$\downarrow$

II. VARIATION OF REDOX PROPERTIES BY PRECIPITATION OF HYDROXIDES

The normal potential of the thallous-thallic system

$$Tl^{3+} + 2e \rightleftharpoons Tl^+$$
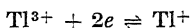
is independent of pH:

$$E = 1·28 + 0·03 \log \frac{|\, Tl^{3+} \,|}{|\, Tl^+ \,|} \text{ volt}$$

This applies until a pH of 0·3 is reached in $10^{-2}M$ solution. After this the s.p. $|\, Tl^{3+} \,| \cdot |\, OH^- \,| = 10^{-43}$ is reached, thallic hydroxide precipitates, thus the Tl^{3+} ions in the solution disappear and the formal potential falls rapidly.

$$E = 1·28 + 0·03 \log \frac{10^{-43}}{|\, OH^- \,|^3} \cdot \frac{1}{|\, Tl^+ \,|}$$

$$= 1·28 + 0·03 \log \frac{10^{-1} \cdot |\, H^+ \,|^3}{|\, Tl^+ \,|} \text{ volts}$$

$$= 1·25 + 0·03 \log \frac{1}{|\, Tl^+ \,|} - 0·09 \, pH$$

We now have the system:

$$Tl(OH)_3 \downarrow + 2e + 3H^+ \rightleftharpoons Tl^+ + 3H_2O$$
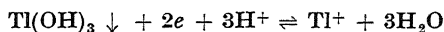
$$E = E'_0 + 0·03 \log \frac{|\, H^+ \,|^3}{|\, Tl^+ \,|} \quad \text{with} \quad E'_0 = 1·25 \text{ volt}$$

The formal potential as a function of pH is presented in fig. 26 for $10^{-2}M$ solutions.

In acid solution, Tl^{3+} is a strong oxidant. In alkaline solution Tl^+ is an energetic reductant.

The same remarks apply to the system Fe^{3+}/Fe^{2+}. Above pH 2 an 0·01M solution starts to precipitate. Fe^{3+} ions disappear as $Fe(OH)_3$ and the formal normal potential falls (fig. 41, p. 164).

Thus Fe^{2+} only oxidizes slowly in the air in acid solution, but more rapidly when Fe^{3+} commences to precipitate. Ferrous salts become energetic reductants when the solution is no longer acid.

Inversely.—Oxidation and reduction with precipitation involve variations in the acidity of the solution. Thus the oxidation of Tl^+ makes the solution more acid.
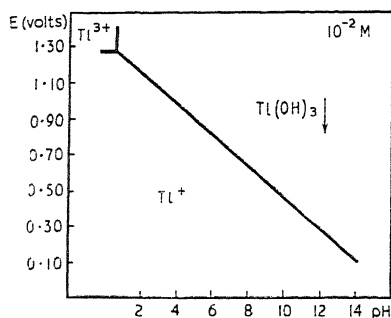
FIG. 26.—FORMAL POTENTIAL OF THE SYSTEM $Tl(III)/Tl(I)$

The same applies to the system

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 \downarrow + 2H_2O$$
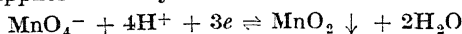
for which we may write

$$E = E_0 + \frac{0\cdot06}{3} \log |MnO_4^-| . | H^+ |^4$$

defining thus a new normal potential E_0.

With the system

$$PbO_2 \downarrow + 2H^+ + 2e \rightleftharpoons PbO \downarrow + H_2O$$
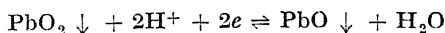
we have
$$E = E_0 - 0\cdot06 \, pH$$

Disproportionation by precipitation of hydroxides.—Consider the system

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$$
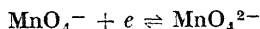
Its normal potential, independent of pH, is represented by the line AB in the adjacent fig. 27.
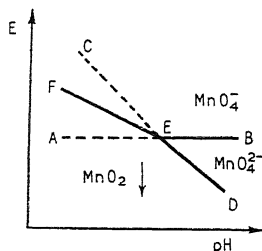
FIG. 27.—FORMAL POTENTIAL OF THE SYSTEMS $MnO_4^{2-}/MnO_4^-/MnO_2$
AS A FUNCTION OF pH

In the system

$$MnO_4^{2-} + 4H^+ + 2e \rightleftharpoons MnO_2 \downarrow + 2H_2O$$
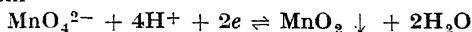
we have
$$E = E_0 + \frac{0\cdot06}{2} \log | H^+ |^4$$

Its formal normal potential varies as $-0.12\ p\mathrm{H}$. It is represented by the line CD. It will be seen that to the left of E the system

$$\mathrm{MnO_4}^{2-}/\mathrm{MnO_2} \downarrow$$
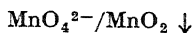
is more oxidizing than the system $\mathrm{MnO_4}^-/\mathrm{MnO_4}^{2-}$. The oxidant of the first system $\mathrm{MnO_4}^{2-}$ reacts on the reductant of the second system $\mathrm{MnO_4}^{2-}$ thus:

$$3\mathrm{MnO_4}^{2-} + 4\mathrm{H}^+ \rightleftharpoons \mathrm{MnO_2} \downarrow + 2\mathrm{MnO_4}^- + 2\mathrm{H_2O}$$
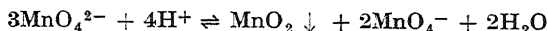
$\mathrm{MnO_4}^{2-}$ disappears by disproportionation, because the low-solubility $\mathrm{MnO_2}$ causes the equilibrium to be displaced towards the right, which comes back to saying that the system $\mathrm{MnO_4}^{2-}/\mathrm{MnO_2} \downarrow$ is more oxidizing in acid solution.

To the left of the point E, $\mathrm{MnO_4}^-$ and $\mathrm{MnO_2}$ remain, and the new system will be

$$\mathrm{MnO_4}^- + 4\mathrm{H}^+ + 3e \rightleftharpoons \mathrm{MnO_2} \downarrow + 2\mathrm{H_2O}$$
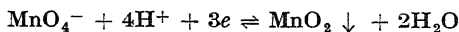
$$\mathrm{E} = \mathrm{E'_0} + \frac{0.06}{3} \log |\, \mathrm{H}^- \,|^4 \text{ Line EF}$$

The regions of predominance of $\mathrm{MnO_4}^{2-}$ and of $\mathrm{MnO_4}^-$, and of appearance of $\mathrm{MnO_2}$, are thus delimited.

Balancing equations.—Consider the disproportionation of the manganates:

$$\mathrm{MnO_4}^{2-} + \ldots \rightleftharpoons \mathrm{MnO_4}^- + \mathrm{MnO_2} \downarrow + \ldots$$
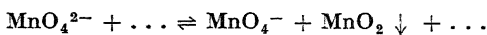
The two redox systems reacting are

$$2[\mathrm{Mn}^{6+} - e \longrightarrow \mathrm{Mn}^{7+}]$$

$$\frac{\mathrm{Mn}^{6+} + 2e \longrightarrow \qquad \mathrm{Mn}^{4+}}{3\mathrm{Mn}^{6+} \quad \longrightarrow 2\mathrm{Mn}^{7+} + \mathrm{Mn}^{4+}}$$

or $\qquad 3\mathrm{MnO_4}^{2-} + 4\mathrm{H}^+ \longrightarrow 2\mathrm{MnO_4}^- + \mathrm{MnO_2} \downarrow + \mathrm{H_2O}$
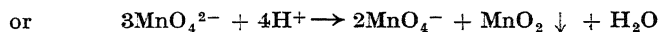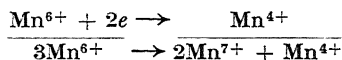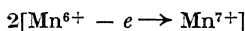
Experiment.—To a few millilitres of 0.01N permanganate add a few millilitres of 0.5N caustic soda, and one or two drops of a 10 per cent sulphite solution. The solution becomes green through reduction of the permanganate to manganate.

Add some acid to this solution: the green manganate disproportionates and the violet colour of the permanganate reappears.

Another example.—Let us plot the formal potentials of 0.01M solutions of the redox systems of Hg as a function of $p\mathrm{H}$. We have

$$2\mathrm{Hg}^{2+} + 2e \rightleftharpoons \mathrm{Hg_2}^{2+}; \quad \mathrm{E} = 0.91 + 0.03 \log \frac{|\, \mathrm{Hg}^{2+} \,|^2}{|\, \mathrm{Hg_2}^{2+} \,|} \text{ volt}$$
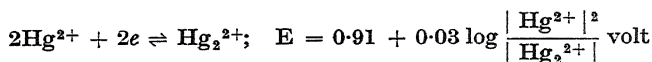
The formal potential is independent of $p\mathrm{H}$. When the $p\mathrm{H}$ increases, low-solubility HgO is formed (at $p\mathrm{H}$ 2 in an 0.01M perchloric acid solution) and we have then

$$2\mathrm{HgO} \downarrow + 4\mathrm{H}^+ + 2e \rightleftharpoons \mathrm{Hg_2}^{2+} + 2\mathrm{H_2O} \quad \mathrm{E} = \mathrm{A} - 0.12\ p\mathrm{H}$$

$$\mathrm{Hg_2}^{2+} + 2e \rightleftharpoons \mathrm{Hg} \downarrow \quad \mathrm{E} = 0.80 + 0.03 \log |\, \mathrm{Hg_2}^{2+} \,| \text{ volt}$$
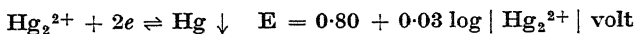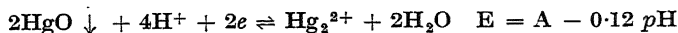
This is shown in fig. 28. It will be seen that the two straight lines intersect at about pH 3. Hg_2^{2+} then disproportionates into Hg and HgO:

$$Hg_2^{2+} + H_2O \rightleftharpoons HgO \downarrow + Hg \downarrow + 2H^+$$

The new system is then

$$HgO \downarrow + 2H^+ + 2e \rightleftharpoons Hg \downarrow + H_2O \quad E = B - 0.06 \, pH$$

The domains of predominance of the various substances are thus determined (see fig. 28). It will be seen that Hg_2^{2+} only exists over a small region of potential and pH. Hg_2O and $Hg_2(OH)_2$ do not exist. If the attempt is made to form them by reduction of HgO, Hg is obtained. If caustic soda is added to Hg_2^{2+} the pH increases and there is a disproportionation into HgO and Hg.
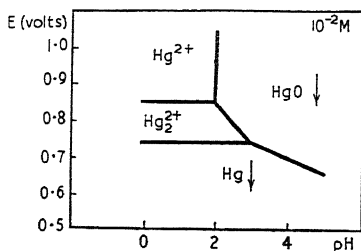
FIG. 28.—APPROXIMATE FORMAL POTENTIALS OF THE SYSTEMS
Hg(II)/Hg(I)/Hg

Region of existence of the states of oxidation.—The existence of certain states of oxidation can be conditioned not only by the redox properties of the solvent, but also by disproportionation reactions.

III. VARIATION OF REDOX PROPERTIES BY PRECIPITATION OF SALTS

(1) **Reducing power of silver in hydrochloric acid solution.**—Silver is a metal which it is difficult to attack since its redox potential is high:

$$Ag \downarrow - e \rightleftharpoons Ag^+ \quad E = 0.80 + 0.06 \log | Ag^+ | \text{ volt}$$
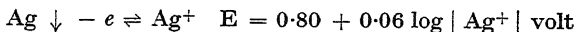
It cannot be oxidized except by energetic oxidizing agents; it is a rather poor reductant.

In the presence of Cl^- ions, matters are different, as a result of the formation of low-solubility AgCl, having the s.p. $| Ag^+ | . | Cl^- | = 10^{-9.7}$. In N-HCl, $| Ag^+ |$ cannot exceed $10^{-9.7}$ and we have

$$E = 0.80 + 0.06 \log 10^{-9.7} = 0.22 \text{ volt}$$

Thus silver, in the presence of chloride ions, becomes much more reducing. In N-HCl it can for example reduce Fe^{3+}.

Reducing power of mercury.—Similar reasoning can be applied. The reducing power of mercury in N-HCl is similar to that of silver, because of the formation of low-solubility Hg_2Cl_2.

(2) **Oxidizing power of cupric salts.**—Cupric ions are not very strong oxidants:

$$Cu^{2+} + e \rightleftharpoons Cu^+ \quad 0 \cdot 17 \text{ volt}$$

$$Cu^{2+} + 2e \rightleftharpoons Cu \downarrow \quad 0 \cdot 35 \text{ ,,}$$
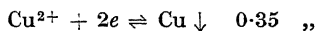
However, they can become considerably more oxidizing if low-solubility cuprous compounds are formed. They can, in particular, oxidize iodides because of the formation of low-solubility CuI.

$$I_2 + 2e \rightleftharpoons 2I^- \quad 0 \cdot 62 \text{ volt}$$

$$Cu^{2+} + 2I^- \longrightarrow CuI \downarrow + \tfrac{1}{2}I_2$$
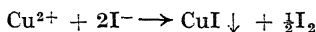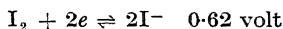
Experiment.—Take a solution of a cupric salt, mix it with an acetate buffer and add a little benzidine (in alcohol or acetic acid). Add some thiocyanate ion CNS^-. Cu^{2+} becomes very oxidizing, because CuCNS is of low solubility. The benzidine is oxidized and a blue colour appears.

(3) **Oxidizing power of ferricyanides.**—Ferricyanides do not oxidize iodides in acid solution. The addition of a zinc salt causes this oxidation to occur quantitatively.

$$E = 0 \cdot 60 + 0 \cdot 06 \log \frac{\mid Fe(CN)_6{}^{3-} \mid}{\mid Fe(CN)_6{}^{4-} \mid} \text{ volt}$$

$$E = 0 \cdot 62 + 0 \cdot 03 \log \frac{\mid I_2 \mid}{\mid I^- \mid^2} \text{ volt}$$

The addition of the zinc salt causes the low-solubility zinc ferrocyanide to be precipitated. The ferrocyanide ions disappear, E rises; ferricyanide becomes more oxidizing, the oxidation of iodides becomes possible.

Summarizing it can be said that the precipitation of one of the ions, whether oxidant or reductant, apparently reinforces the reducing or oxidizing properties of the conjugate ion.

Oxidizability of sulphides.—The oxidation of sulphides in the presence of water obeys the relationship:

$$E = E_0 - 0 \cdot 03 \log \mid S^{2-} \mid$$

When a sulphide is of low solubility, S^{2-} is limited by its s.p. The smaller S^{2-}, the larger E and hence the more difficult the sulphide is to oxidize.

Referring to the s.p.'s of the sulphides we have, for example:

$$\mid Hg^{2+} \mid . \mid S^{2-} \mid = 10^{-53}$$

$$\mid Ag^+ \mid^2 . \mid S^{2-} \mid = 10^{-49}$$

$$\mid Fe^{2+} \mid . \mid S^{2-} \mid = 10^{-22}$$

$$\mid Mn^{2+} \mid . \mid S^{2-} \mid = 10^{-15}$$

It will be seen that mercuric sulphide is the least easy to oxidize. It is not attacked by nitric acid at $100°$ C. Silver sulphide is attacked slowly by hot nitric acid. The wet sulphides of manganese and iron are oxidized on exposure to the air. Soluble sulphides such as those of the alkali metals oxidize in the air.

Reduction of mercuric salts in hydrochloric acid solution.—Mercuric salts in acid solution are reduced by the majority of reductants

8

to metallic mercury, without a halt at the mercurous stage; the potentials of the two systems are very near to one another: 0·91 and 0·80 volt.

In hydrochloric acid, Hg_2Cl_2 is of low solubility and thus Hg^{2+} becomes more oxidizing and Hg^+ more reducing, and thus the stage of Hg_2Cl_2 is more easily halted at. Thus stannous chloride in restricted quantity reduces mercuric salts, giving a white precipitate of mercurous chloride.

Existence of higher oxides.—The oxides of higher odixation number generally yield unstable cations which are either too acid or too oxidizing. The very low solubility of the oxide stabilizes the corresponding oxidation state. In spite of this low solubility, the higher oxides are often very strongly oxidizing.

$$PbO_2 \quad Pb^{2+} \quad E_0 = 1·47 \text{ volt at } pH \ 0$$

$$MnO_2 \ Mn^{2+} \quad E_0 = 1·28 \text{ volt at } pH \ 0$$
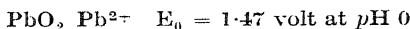
Disproportionation.—(1) **Disproportionation is favoured by precipitation, which displaces the equilibrium.**

Example.—(a) ClO^- disproportionates very slowly into ClO_3^- and Cl^-, but rapidly in the presence of Ag^+ ions.

$$3ClO^- + Ag^+ \rightleftharpoons ClO_3^- + 2AgCl \downarrow$$
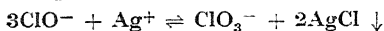
(b) $S_2O_3^{2-}$ disproportionates, along the same lines, into SO_4^{2-} and S^{2-} even in neutral solution, in the presence of Hg^{2+} ions.

$$S_2O_3^{2-} + Hg^{2+} + H_2O \longrightarrow HgS \downarrow + SO_4^{2-} + 2H^+$$
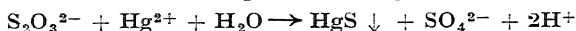
and the solution becomes acid.

Note.—Yellowish mercuric chlorosulphide is formed as an intermediate compound.

Detection of thiosulphates.—This reaction is utilized for the detection of thiosulphates (p. 121). Add a drop of methyl orange to a drop of thiosulphate solution (which is neutral because $HS_2O_3^-$ is a fairly strong acid). Then add neutral mercuric chloride in excess. The solution becomes acid and the indicator turns red.

(c) Iodine disproportionates in the presence of Ag ions as a result of the formation of low-solubility AgI, even in acid solution.

$$I_2 + Ag^+ + H_2O \longrightarrow HIO + AgI \downarrow + H^+$$

or $$3I_2 + 3H_2O + 5Ag^+ \longrightarrow IO_3^- + 5AgI \downarrow + 6H^+$$
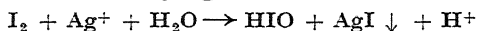
Experiment.—Add a drop of iodine in iodide solution to a little water: then a little starch which turns blue with the iodine present. Add silver nitrate drop by drop: the blue colour of the iodine disappears.

(2) **Disproportionation can be inhibited by the formation of low-solubility compounds.**—Cu^+ scarcely exists in water because of disproportionation, but low-solubility compounds such as CuI, $CuCl$, Cu_2O are known.

(3) **Intermediate hydroxides.**—When the element has several states of oxidation, intermediate hydroxides or oxides are generally formed in alkaline solution: such as Fe_3O_4 (or $Fe(FeO_2)_2$), Pb_3O_4, etc. These oxides are disproportionated in acid solutions.

PRECIPITATION. COMPLEXES. REDOX AND pH

WE give below some more complicated examples which involve the exchange of more than two species of particles.

Attack of metals by the formation of complexes.—*Example.*—
(*a*) *Gold is a noble metal.* $E = 1.46 + 0.06 \log | Au^+ |$ volts.

Only very powerful oxidants can attack it. However, in the presence of cyanides, it oxidizes rapidly in the air and passes into solution; in effect, an aurocyanide complex of great stability is formed; $| Au^+ |$ thus becomes very small in the presence of CN^- ions. E decreases rapidly and the gold then oxidizes easily in the air, and very rapidly in the presence of oxidizing agents.

(*b*) *Attack by HF.*—The fluoride ion forms complexes with a large number of ions. This explains the attack of certain metals by hydrofluoric acid which is actually a weak acid. Thus tantalum, a metal which is attacked only with difficulty, is oxidized in the presence of hydrofluoric acid as a result of formation of a fluoride complex. Naturally, the attack is favoured in all cases by the addition of an oxidant. Attack by a mixture of nitric and hydrofluoric acids is still more efficacious.

(*c*) *Attack of antimony by mixed nitric and tartaric acids.*

(*d*) *Attack by aqua regia.*—Aqua regia is a mixture of concentrated HCl and HNO_3. It should not obviously be more oxidizing than HNO_3 itself. However, attack is favoured by the formation of chloride complexes. This is the case with gold and the metals of the platinum group which give stable chloride complexes.

$$3Pt \downarrow + 4NO_3^- + 18Cl^- + 16H^+ \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$
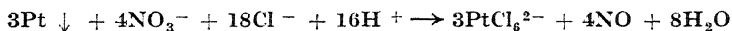
(*e*) *A piece of silver foil blackens in damp air, in the presence of traces of hydrogen sulphide.*—Black silver sulphide of very low solubility is formed:

$$| Ag^+ |^2 . | S^{2-} | = 10^{-45.8}$$

Thus silver is oxidized:

$$Ag \downarrow - e \rightleftharpoons Ag^+ \quad E = 0.80 + 0.06 \log | Ag^+ |\ \text{volt}$$
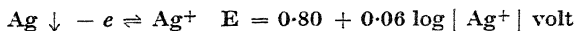
The oxidizing systems can be H^+ due to H_2S:

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow \quad E = -0.06\ pH \quad . \quad . \quad . \quad \text{(I)}$$

or atmospheric oxygen:

$$O_2 \uparrow + 4H^+ + 4e \rightleftharpoons 2H_2O \quad E = 1.23 - 0.06\ pH\ \text{volt} \quad . \quad . \quad \text{(II)}$$
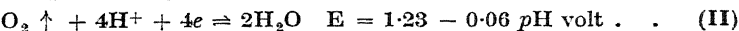
We have

$$\frac{| HS^- | . | H^+ |}{| H_2S |} = 10^{-7.1} \quad \text{and} \quad \frac{| S^{2-} | . | H^+ |}{| HS^- |} = 10^{-14.9}$$

whence

$$\frac{| S^{2-} | . | H^+ |^2}{| H_2S |} = 10^{-22}$$

The solubility of H_2S is about 0.1M.

Let us find out first exactly which is the system which has oxidized the silver. The pH is determined by H_2S:

$$pH = \tfrac{1}{2}pK - \tfrac{1}{2}\log c = 3 \cdot 5 + 0 \cdot 5 = 4 \cdot 0$$

System (I) has a potential of $E = -0 \cdot 06\, pH = -0 \cdot 24$ volt. System (II) gives a potential of $E = 1 \cdot 2 - 0 \cdot 06\, pH = 0 \cdot 96$ volt.

Silver becomes strongly reducing in the presence of S^{2-} on account of the formation of Ag_2S of very low solubility. At pH $4 \cdot 0$ $|\,S^{2-}\,|$ is given by $\dfrac{|\,S^{2-}\,| \cdot (10^{-4})^2}{|\,10^{-1}\,|} = 10^{-22}$; thus $|\,S^{2-}\,| = 10^{-15}$.

$|\,Ag^+\,|$ is given by the s.p. : $|\,Ag^+\,|^2 . 10^{-15} = 10^{-48 \cdot 8}$ whence $|\,Ag^+\,| = 10^{-16 \cdot 9}$ and the reducing power of silver is given by $E = 0 \cdot 80 + 0 \cdot 06\log 10^{-16.9} = -0 \cdot 21$ volt.

Oxidation thus occurs via the oxygen of the air. It is slow, because the system with oxygen acts slowly.

We thus have the reaction:

$$O_2 \uparrow + 2H_2S \uparrow + 4Ag \downarrow \longrightarrow 2Ag_2S \downarrow + 2H_2O$$
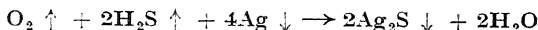
Action of ammonia on mercurous chloride. Detection of mercurous mercury and of Ag^+:

$$Hg_2Cl_2 \downarrow + 2NH_3 \longrightarrow HgNH_2Cl \downarrow + Hg \downarrow + NH_4^+ + Cl^-$$
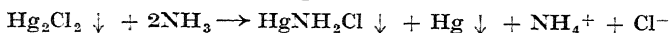
Mercuric aminochloride and black metallic mercury are formed.

This reaction involves two disproportionations:

$$Hg_2^{2+} \longrightarrow Hg^{2+} + Hg \downarrow$$

and

$$2NH_3 \longrightarrow NH_2^- + NH_4^+$$
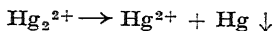
NH_2^- is extremely basic and can only exist in compounds which are only very slightly ionized: e.g. $HgNH_2Cl$.

Naturally, the addition of acid reproduces NH_3 and then NH_4^+ and the compound has a tendency to redissolve.

Usually when Hg_2^{2+} and Ag^+ are being sought, they are precipitated in the form of their chlorides which are washed. The precipitate is taken up again with NH_3. $AgCl$ passes into solution in the form of an amminated complex and $HgNH_2Cl$ + black Hg remain on the filter. Thanks to the NH_4^+ a little of the aminochloride can redissolve.

$$HgNH_2Cl \downarrow + NH_4^+ \longrightarrow 2NH_3 + HgCl^+$$
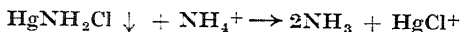
CHAPTER XV

SOLVENTS OTHER THAN WATER

SOLVENTS other than water offer various possibilities, because the properties of compounds are different in them and, as a result, reactions can be realized which are impossible in water: all the constants are different as well as the solubilities: the limitations relative both to ions and states of oxidation are also different.

Certain rules make it possible to predict qualitatively a certain number of properties starting from the properties in aqueous solution. (See *Methodes Modernes d'Analyse Quantitative*, G. Charlot and D. Bezier, Masson, Paris, 1949.)

EXCHANGE OF PROTONS.—(*a*) **Protolytic solvents.**—These solvents behave in a manner similar to water. They can play the role of acid and of base in relation to proton exchange.

Thus alcohol C_2H_5OH gives the following acid-base equilibria:

$$C_2H_5OH + H^+ \rightleftharpoons C_2H_5OH_2^+$$
$$C_2H_5OH - H^+ \rightleftharpoons C_2H_5O^-$$
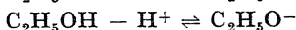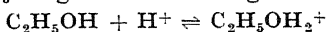
The ionic product, similar to that for water, is given by:

$$2C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$$
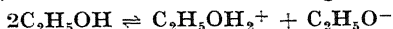
i.e. $\qquad | C_2H_5OH_2^+ |.| C_2H_5O^- | = 10^{-19}$

Pure acetic acid gives

$$CH_3CO_2H + H^+ \rightleftharpoons CH_3CO_2H_2^+$$

and $\qquad CH_3CO_2H - H^+ \rightleftharpoons CH_3CO_2^-$
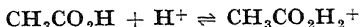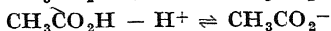
Ionic product: $\qquad | CH_3CO_2H_2^+ |.| CH_3CO_2^- | = 10^{-10}$

Alcohols and acids are protolytic solvents.

Liquid ammonia considered as a solvent gives

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$NH_3 - H^+ \rightleftharpoons NH_2^-$$
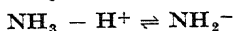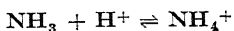
Note.—The two acid-base systems of the solvent limit the two extremes of the acidity scale.

For example, in acetic acid, any acid stronger than $CH_3CO_2H_2^+$ will be a strong acid:

$$HClO_4 + CH_3CO_2H \rightarrow ClO_4^- + CH_3CO_2H_2^+$$
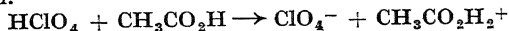
Any base stronger than $CH_3CO_2^-$ will be a strong base:

$$NH_3 + CH_3CO_2 \rightarrow NH_4^+ + CH_3CO_2^-$$
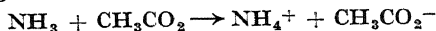
The strength of acid-base pairs and the acidity of the solution can be determined by means of acidity potentials. pK values and a pH scale defined by analogy with that which is generally adopted for water can be used:

$$\frac{| \text{Base} |.| H^+ \text{ solvated} |}{| \text{Acid} |} = K; \quad pH = - \log | H^+ \text{ solvated} |$$

The relative strengths of acid-base pairs in different solvents can be different from what they are in water. They depend both on the basicity of the solvent and its dielectric constant.

(*b*) **Active non-protolytic solvents.**—These can solvate certain ions, but do not naturally donate protons. Frequently they cannot accept them at all. But acids and bases in solution can exchange protons. Thus, in nitrobenzene, we have

$$HCl + C_6H_5NH_2 \longrightarrow C_6H_5NH_3^+ + Cl^-$$
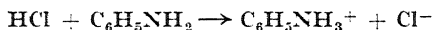
The acidity scale has no limit.

(*c*) **Inert solvents.**—Proton exchange can still occur, but the reactions take place between molecules:

$$HCl + NH_3 \longrightarrow NH_4Cl$$
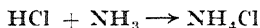
EXCHANGE OF IONS.—(*a*) **Active solvents.**—The solvent can exchange a given particle.

Thus $COCl_2$ can exchange Cl^-:

$$COCl_2 \rightleftharpoons COCl^+ + Cl^-$$

and $$COCl_2 + Cl^- \rightleftharpoons COCl_3^-$$
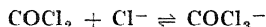
We thus get reactions such as

$$AlCl_3 + COCl_3^- \rightleftharpoons AlCl_4^- + COCl_2$$
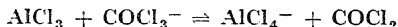
In simplified notation, that is, omitting the molecules of the solvent, the reaction becomes

$$AlCl_3 + Cl^- \longrightarrow AlCl_4^-$$
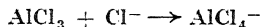
Thus there are limitations of the scale for the Cl^- donor-acceptor systems.

(*b*) **Inert solvents.**—These do not take part in reactions between complexes.

REACTIONS IN THE PRESENCE OF A SECOND SOLVENT. EXTRACTION

THE most interesting case is that in which one of the solvents is water and the other is an organic liquid insoluble in water: benzyl alcohol, carbon tetrachloride, chloroform, ether, ethyl acetate, etc.

Certain inorganic compounds are soluble in these organic solvents (thiocyanates, chlorides, etc.). Numerous organic-inorganic compounds dissolve in them.

Distribution coefficients.—When a substance A is soluble both in the solvent and in water, the equilibrium
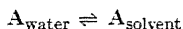
$$A_{water} \rightleftharpoons A_{solvent}$$

is set up, and, applying the law of mass action, we get the expression:

$$\frac{|\,A\,|\,_{solv.}}{|\,A\,|_{H_2O}} = D$$

D is called the 'Distribution (or sometimes "Partition") coefficient' for the compound considered, between the second solvent and water.

When the two solutions are saturated, equilibrium is still set up, and, as a result, $D = S_s/S_w$, the S's being the solubilities of the substance in the solvent and water.

Note.—If one of the solvents is inert, which frequently happens, the solvent only contains molecules, and these molecules are in equilibrium with those in the water, or with the corresponding ions.

Displacement of the equilibria in water by the addition of a second solvent.—(1) Take for example the equilibrium
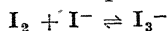
$$I_2 + I^- \rightleftharpoons I_3^-$$

we have

$$\frac{|\,I_2\,|\,.\,|\,I^-\,|}{|\,I_3^-\,|} = K$$

If a second solvent in which the iodine can dissolve is added, the equilibrium will be displaced towards the left and we shall have the additional relationship:

$$I_{2\,H_2O} \rightleftharpoons I_{2\,solv.} \quad \text{with} \quad \frac{|\,I_2\,|_{solv.}}{|\,I_2\,|_{H_2O}} = D$$

Reciprocally, the addition of I^-, or the disappearance of I^-, in the aqueous solution displaces the equilibria and the concentration of iodine in the solvent will vary.

(2) Oxine is an acid:

$$Oxine \rightleftharpoons Ox^- + H^+ \quad \text{with} \quad \frac{|\,Ox^-\,|\,.\,|\,H^+\,|}{|\,Oxine\,|} = K_1$$
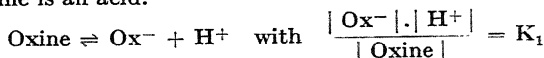
In the presence of a second solvent such as chloroform we have

$$Oxine_{H_2O} \rightleftharpoons Oxine_{CHCl_3} \quad \text{with} \quad \frac{|\,Oxine\,|_{CHCl_3}}{|\,Oxine\,|_{H_2O}} = D$$
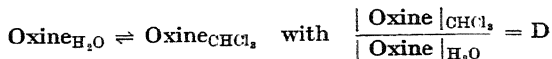
The oxine can be caused to disappear by adding chloroform to the aqueous solution, and the solution becomes less acid as a result.

Reciprocally, the addition of acid to the aqueous solution increases the quantity of oxine in the chloroform (in a solution of low acidity, because oxine is also a base), hence the proportion of oxine dissolved in the chloroform depends on the pH.

(3) Fe^{3+} gives various complexes with CNS^-. $Fe(CNS)_3$ (or $Fe[Fe(CNS)_6]$) is soluble in organic solvents; equilibria are accordingly displaced and complexes in water such as $FeCNS^{2+}$ disappear by disproportionation.

Importance of solvents not miscible with water.—The use of solvents immiscible with water constitutes a new means of affecting in a definite manner the usual equilibria: acid-base, redox, and those involving complexes and precipitation. It is a technique as important as that of the formation of complexes, or precipitation. If this new technique is combined with the ones we already have at our disposal: control of pH, oxidation-reduction, formation of complexes and of precipitates, the possibilities open to us are boundless. It should be added that a large number of compounds between inorganic ions and organic reagents are soluble in solvents which are not miscible with water.

We do not intend to develop here these possibilities in the same detail as has been done for aqueous systems in the preceding chapters: the methods of reasoning are similar, and the chemist already familiar with them can easily envisage their application to the various cases which present themselves.

Extraction of a compound from its aqueous solution by means of a second solvent.—Take the simple case of a compound which does not ionize either in water or the other solvent. Let c_0 be the initial concentration in a volume V of water. The total quantity of material is c_0V. Add to this a quantity V′ of the second solvent, and when equilibrium has been attained, let c_1 be the concentration of the substance in water, and c'_1 its concentration in the solvent. We shall have the relations:

$$\frac{c'_1}{c_1} = D \quad \text{and} \quad c_0V = c_1V + c'_1V' \quad \text{whence} \quad c_1 = \frac{c_0V}{V + DV'},$$

Remove the solvent and repeat the operation with the same volume of pure solvent. After n operations of this kind, we have

$$c_n = c_0\left(\frac{V}{V + DV'}\right)^n$$

c_n being the concentration in water after n extractions. If $D = 10$, that is to say if the compound is 10 times more soluble in the solvent than it is in water, we have for the case where $c_0 = 100$ and $V = V'$:

$$c_1 = 9; \quad c_2 = 0.8; \quad c_3 = 0.07$$

If D were 1000, extraction would be complete (99·9 per cent) after a single operation.

The ratio V/V' changes in the same way as D.

Technique of extraction in qualitative analysis.—Equilibrium is only attained between the two phases in general after vigorous shaking, and when the concentrations are small, the shaking must be prolonged.

Usually, in qualitative analysis, this shaking is done in a test-tube whose mouth is closed by the finger. If the system be then filtered through a filter paper wetted in advance with water, the aqueous solution will pass through; if it is desired to get the solvent phase to pass through, then the filter should be wetted with the pure solvent. After separation, the phase which remains on the filter can be washed with some of the other solvent.

If filtration appears impracticable, then separating funnels can be used; this facilitates the washing of the phases.

Examples are given in Part II (see Aluminium, p. 157).

SLOW REACTIONS. REACTIONS EFFECTED IRREVERSIBLY. CATALYSIS

SLOW REACTIONS

THE parameters which have been defined in the preceding chapters and the information about the constants of different systems permit the prediction of the equilibria which should be obtained when several substances are mixed.

Sometimes reactions are slow and we cannot wait for equilibrium to be attained: sometimes the reactions are so slow that to all intents and purposes they do not occur ('false equilibria'). The preceding considerations then merely enable us to predict what is theoretically possible but they are insufficient to tell us whether what we predict can really be achieved on our time scale.

Fortunately the majority of reactions involving exchanges of ions are rapid. However, a considerable number of oxidation and reduction reactions are slow.

Redox reactions

A certain number of redox reactions are rapid and the final equilibrium is predictable by means of redox potentials. This is the case for reactions between two systems among the following: $Fe(III)/Fe(II)$— $Ce(IV)/Ce(III)$ — $Hg(II)/Hg(I)$ — I_3^-/I^- — $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ — $Zn(II)/Zn \downarrow$ —$Cd(II)/Cd \downarrow$ —$Cu(II)/Cu \downarrow$ —$Pb(II)/Pb \downarrow$ —$Ag(I)/Ag \downarrow$, and without doubt among others as well.

This should be the case also for numerous other systems for which the rate of reaction is increased by means of catalysts, by raising the temperature, changing the pH, etc.

In numerous other cases reactions are slow or infinitely slow in the neighbourhood of equilibrium, and whilst the rate of reaction depends on both the substances present it can be said that certain substances are always reduced or oxidized infinitely slowly in dilute solutions: ClO_4^-, SO_4^{2-}, etc. The systems in water

$$2H_2O - 4e \rightleftharpoons O_2 + 4H^+ \quad E = 1 \cdot 23 - 0 \cdot 06 \, pH \text{ (volts)}$$

and $\quad 2H_2O + 2e \rightleftharpoons H_2 + 2OH^- \quad E = -0 \cdot 06 \, pH \text{ (volts)}$
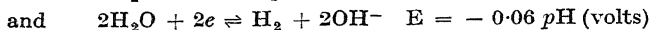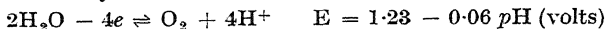
only react very slowly in the neighbourhood of equilibrium, so that numerous substances exist in solution which should oxidize or reduce water: MnO_4^- (1·6 volts at pH 0), Cr^{2+} ($-0 \cdot 5$ volt at pH 0), etc.

Oxidation and reduction potential. Reactions carried out irreversibly.— Take for example the redox system sulphite-dithionate:

$$2SO_3^{2-} - 2e \rightleftharpoons S_2O_6^{2-}$$
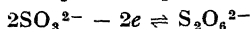
The normal potential of this system can be calculated and we have

$$E = -0 \cdot 3 + 0 \cdot 03 \log \frac{| \, S_2O_6^{2-} \, |}{| \, SO_3^{2-} \, |^2} \text{ volt}$$

If we consider a solution containing unit concentration of SO_3^{2-} and $S_2O_6^{2-}$, all systems whose potential is higher than -0.3 volt should oxidize SO_3^{2-}; but none does. In general, oxidants whose potential is already high, Fe(III), I_2 for example, are necessary in order to get reaction at a reasonable speed. We can define very crudely a potential above which SO_3^{2-} will be oxidized at a reasonable speed. It will be called the oxidation potential in order to distinguish it from the redox potential which corresponds to equilibrium. The additional potential difference which is necessary to get reaction at a reasonable speed is analogous to an over-potential.

Note.—It is evident that the oxidation potential, which depends upon the rate of reaction, depends not only on the system considered but also on the two substances reacting. This value of the potential is thus only an indication; exceptions are known. Experience shows that this approximation is very valuable in default of other information.
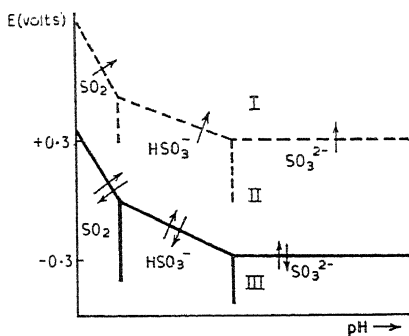
FIG. 29.—EQUILIBRIUM POTENTIAL OF $SO_3^{2-}/S_2O_6^{2-}$
AND OXIDATION POTENTIAL OF SO_3^{2-}

As the oxidation of sulphites cannot take place at a reasonable speed except at a potential very far from the equilibrium potential, the rate of reduction of dithionate is thus negligible. The reaction is carried out irreversibly and the concentration of dithionate has no influence on it. The oxidation potential can be given in the form E (oxidation) $= +0.3 - A \log |SO_3^{2-}|$ volt. The potentials are plotted in fig. 29 as a function of pH. The equilibrium potential is indicated by the solid lines and the oxidation potential by dotted lines. In zone II sulphite is oxidized infinitely slowly or very slowly and is in false equilibrium. In zone I it is oxidized irreversibly. In zone III it cannot be oxidized.

Note.—In electrochemistry the over-potential depends on the nature of the electrode, here it depends on the substances reacting. The chemical reactions which occur in the presence of the electrode material can be rigorously predicted from polarization curves.

Prediction of reactions.—Within the limits of value of these empirical considerations we can get an idea about the conditions under which chemical reactions are possible at a reasonable speed. Let us represent the properties of some systems graphically.

Redox systems of water.—Water can be oxidized:

Overall system: $2H_2O - 4e \rightleftharpoons O_2 + 4H^+$ with $E = 1.23 - 0.06\,pH$ volts

Inversely oxygen can be reduced when the operations are carried out in air.

Water can be reduced:

$$2H^+ + 2e \rightleftharpoons H_2$$
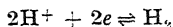
or $\quad 2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$ with $E = -0.06\,pH$ volt

These systems are always operative in aqueous solution and as a result they restrict the region in which reactions are possible.
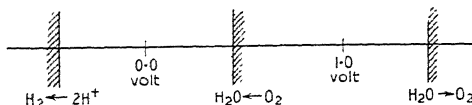
FIG. 30

Example.—Consider the systems:

thiosulphate/tetrathionate $S_2O_3{}^{2-}/S_4O_6{}^{2-}$ and iodine/iodide $I_3{}^-/I^-$.
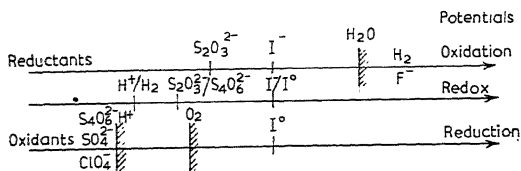
FIG. 31

It can be seen that the thiosulphate can be oxidized at a considerable rate by the iodine. On the other hand $S_4O_6{}^{2-}$ cannot be reduced in aqueous solution: H^+ is reduced beforehand. Thus $S_2O_3{}^{2-}$ cannot be obtained by reduction of $S_4O_6{}^{2-}$ in aqueous solution.

Hydrogen H_2 reacts more slowly than water as a reductant: if it is desired to oxidize it, water is immediately oxidized.

$SO_4{}^{2-}$, $ClO_4{}^-$, H_3PO_4, etc., cannot be reduced, and H_2, F^-, etc., cannot be oxidized in aqueous solution.

It emerges also that numerous substances are in false equilibrium in aqueous solution. Most non-metallic derivatives belong to this group. Thus $ClO_3{}^-$, $ClO_2{}^-$, Cl_2 should disproportionate, but the reaction is infinitely or at least very slow. The majority of organic compounds belong to this class also.

Factors affecting the speed of reaction (or the over-potential)

(1) Raising the temperature diminishes the over-potential.

The redox potential changes when the temperature changes but the over-potential decreases when the temperature increases. Thus conc. sulphuric acid becomes oxidizing when hot. 10N perchloric acid oxidizes at its b.p. (200° C.).

(2) The over-potential may depend on *p*H.—Thus the majority of oxidants containing oxygen atoms have a low over-potential in very acid solution. The over-potential increases and sometimes becomes quite

large when the pH increases. This is the case with NO_3^-, ClO_3^-, BrO_3^-, IO_3^-, H_3AsO_4, etc.

(3) There are some rules relative to the constitution of substances.

Systems involving a simple exchange of electrons in general do not have over-potentials:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}; \quad Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$$
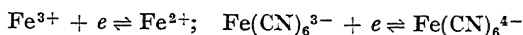
When electron exchange requires a molecular rearrangement, the over-potential is in general important particularly when covalent bonds have to be broken:

$$NO_3^- \longrightarrow NO_2^-, \quad SO_4^{2-} \longrightarrow SO_3^{2-}$$
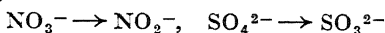
For a given element, in general the over-potential is the greater, the higher the oxidation number.

Examples.—(1) Acids derived from chlorine: Hypochlorous acid, $HClO(Cl(I))$, reacts without a large over-potential both in acid and alkaline solution.

$ClO_3^-(Cl(V))$ does not react except in very acid solution and its rate of reaction is then low.

$ClO_4^-(Cl(VII))$ is not reduced in dilute solution even at high acidity. It is only in concentrated acid solution and in the hot that there is any considerable reduction. However, very powerful reductants such as V^{2+}, Zn, reduce it very slowly in very acid solution.

(2) Nitric acid is not in general reduced except in very acid solution or in the presence of extremely energetic reductants.

Nitrous acid reacts as an oxidant much more rapidly, although its equilibrium potential is lower.

CATALYSIS

Some slow reactions can be accelerated by the presence of small quantities of a suitable redox system.

Example.—In acid solution, arsenious acid reacts slowly with some very powerful oxidants like ceric salts and permanganates:

$$As(III) + 2Ce(IV) \longrightarrow 2Ce(III) + As(V) \text{ (slow)} \quad . \quad . \quad (I)$$
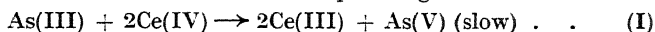
In the presence of a little iodine the reaction becomes rapid. We then have the sequence of rapid reactions:

$$2Ce(IV) + I_2 \longrightarrow 2Ce(III) + 2I^0(I) \quad \text{(fast)} \quad . \quad . \quad (II)$$
$$2I^0(I) + As(III) \longrightarrow As(IV) + I_2 \quad \text{,,} \quad . \quad . \quad (III)$$
$$\overline{2Ce(IV) + As(III)} \longrightarrow \overline{2Ce(III) + As(V)} \quad \text{,,}$$
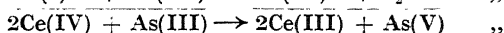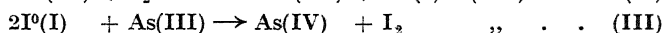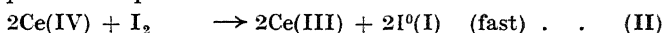
in the presence of iodine.

The oxidation and reduction potentials corresponding to these properties are set out below:

I^0		As(III)		Ce(III)	
	As(V)/As(III)		$I^0I(I)$	Ce(IV)/Ce(III)	oxidation
					redox
	0·5 volt		1·0 volt	1·4 volts	
As(V)	Ce(IV)		I(I)		reduction potentials

The conditions under which catalysis occurs are thus the following:

(1) The odixation-reduction potential of the catalyst system must lie between those of the two reacting systems.

(2) The catalyst system reacts very rapidly in both directions.

Another example.—

$$S_2O_8{}^{2-} + 2e \rightleftharpoons 2SO_4{}^{2-} \quad E_0 = 2 \cdot 05 \text{ volts}$$
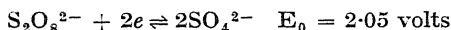
$S_2O_8{}^{2-}$ is thus a very powerful oxidant: but in general it only reacts rapidly when the over-potential is pretty large, about 1 volt. However, it oxidizes Ag^+ and the system Ag^{2+}/Ag^+ (1·98 volts) reacts very rapidly in both directions, thus facilitating numerous oxidations with persulphates, e.g. of Mn^{2+} to $MnO_4{}^-$ and Ce^{+3} to Ce^{4+}.

$$Ag^{2+}/Ag^+ \quad E_0 = 1 \cdot 98 \text{ volts}$$
$$Ce^{4+}/Ce^{3+} \quad E_0 = 1 \cdot 45 \quad ,,$$

and we have

$$
\begin{array}{ll}
S_2O_8{}^{2-} + 2Ag^+ \rightarrow 2SO_4{}^{2-} + 2Ag^{2+} & \text{fairly fast} \\
2Ag^{2+} + 2Ce^{3+} \rightarrow 2Ag^+ + 2Ce^{4+} & \text{fast} \\
\hline
S_2O_8{}^{2-} + 2Ce^{3+} \rightarrow 2SO_4{}^{2-} + 2Ce^{4+} & \text{fairly fast in presence of } Ag^+
\end{array}
$$
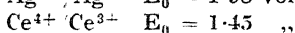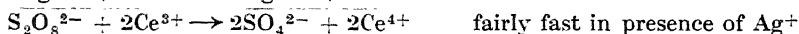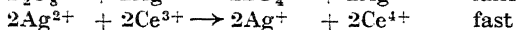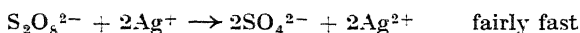
The reactions are carried out hot in order to increase their rate. Without a catalyst they practically do not occur.

Examples of catalysts

It follows from what has been said above that a given catalyst system has a more general applicability according as its oxidation potential is smaller in relation to the corresponding reduction potential.

Catalyst system	*Reactions catalysed*
Ag(II)/Ag(I) 1·98 volts at $pH = 0$ . . .	$S_2O_8{}^{2-} + Mn(II)$ $S_2O_8{}^{2-} + Cr(III)$, etc.
$I^- \cdot I^0 \cdot I(I) \cdot I(V)$	$As(V) + SO_2$ $As(III) + MnO_4{}^-$ $As(III) + Ce(IV)$ $ClO_4{}^- + Sn(II)$
Re(VII)/Re(V)	$ClO_4{}^- + Sn(II)$ $As(V) + SO_2$ $NO_3{}^- + Sn(II)$ $SO_4{}^{2-} + Sn(II)$
Os(VIII)/Os	$ClO_3{}^- + Fe(II)$ $As(III) + MnO_4{}^-$
Mo(VI)/Mo(V)	$NO_3{}^- + Fe(II)$
$NiO_2/Ni_2O_3/Ni_3O_4$ CoO_2/Co_2O_3 $\}$	$OH^- + ClO^-$
Hg(II)/Hg	$H_3PO_2 + H^+$
Finely divided Pt/Pt(II) ,, ,, Pd/Pd(II) $\}$	Very many reactions

ION EXCHANGE REACTIONS

Reactions involving the exchange of protons and even ions are generally fast in homogenous media.

However, certain stable complexes can be formed very slowly, for example ferrous *o*-phenanthroline, the cobalticyanide ion, etc.

HYDRATION-CONDENSED IONS

Hydration and dehydration reactions involving condensed ions are frequently slow.

(1) Take the case of the acids derived from $P(V)$; H_3PO_4, orthophosphoric acid, and $H_4P_2O_7$, pyrophosphoric acid. We have the equilibrium:

$$H_4P_2O_7 + H_2O \rightleftharpoons H_3PO_4$$
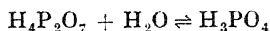
Theoretically the equilibrium is practically completely displaced to the right: $H_4P_2O_7$ should not exist in solution. However, it can be prepared in the dry way, under which condition it is stable. When it is then introduced into aqueous solution, it only hydrates to the ortho acid extremely slowly. The above equilibrium, whose attainment would involve the more or less complete disappearance of the pyro acid, is only realized after a long time of boiling and in acid solution.

(2) In a solution of a vanadate, at pH 7–9, the colourless $H_2VO_4^-$ ion predominates: addition of acid causes the formation of the orange $H_3V_2O_7^-$:

$$2H_2VO_4^- + H^+ \longrightarrow H_3V_2O_7^- + H_2O$$
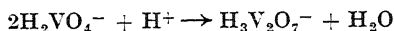
The reverse reaction is extremely slow, so that when caustic soda is added to the orange solution, it remains orange. Decoloration can only be produced by prolonged heating.

(3) Numerous condensed ions are formed, especially by the elements of the fifth and sixth groups of the periodic table. The non-metals S, P, B, Si, also yield condensed ions. The chemistry of these elements is complicated by the instability of many of these bodies.

PRECIPITATION REACTIONS

We have seen (p. 67) that precipitation and the properties of precipitates depend upon time, and the equilibria are sometimes attained only slowly, sometimes indeed infinitely slowly. It is for this reason that we were led to define several apparent solubility products for the same substance.

As a result, in the course of the ageing of a precipitate, its redox properties, the properties of its complexes, and the pH can change.

Inversely, the dissolution of precipitates by redox, by adjustment of the pH and by the formation of complexes depends on the degree of ageing of the solids concerned.

In addition, the redissolution of precipitates can be slow, sometimes very slow.

Induced precipitation.—

EXTRACTION

The establishment of equilibrium between two phases sometimes takes a very long time to attain. Sometimes the exchange is rapid in one direction, and slow in the other.

Thus at pH 2, aluminium oxinate dissolved in chloroform only passes very slowly into water. At $pH = 0$, the equilibrium, which is then much more displaced, is attained rapidly.

General note.—In every case parameters similar to overvoltage can be defined, and similar arguments can be applied as to redox reactions, including cases of catalysis.

CHAPTER XVIII

INDICATORS AND REAGENTS

I. INDICATORS

INDICATORS are systems which reveal changes in their state by very easily apprehended changes in their properties, such as colour. These changes in the state of an indicator can be brought about by changes in the concentrations of ions in the solution in which they are present. They can therefore be used to determine these concentrations.

An indicator consists of a donor-acceptor system:

$$\text{Acceptor}_2 + p \rightleftharpoons \text{Donor}_2 \quad \ldots \quad \text{(I)}$$
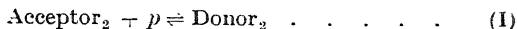
The acceptor and the donor have different colours. The colour of the solution is thus characteristic of the ratio of the concentrations of the two coloured forms $|\text{Acceptor}_2|/|\text{Donor}_2|$.

By exchanging the particle involved with another system, equilibria such as

$$\text{Donor}_1 + \text{Acceptor}_2 \rightleftharpoons \text{Acceptor}_1 + \text{Donor}_2 \quad \ldots \quad \text{(II)}$$
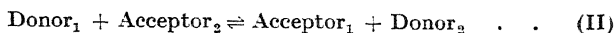
are set up, for which

$$\frac{|\text{Acceptor}_1|.|\text{Donor}_2|}{|\text{Donor}_1|.|\text{Acceptor}_2|} = K \quad \ldots \quad \text{(III)}$$

The colour of the indicator system must be sufficiently strong that only a trace of it is necessary to give an easily detected coloration. Thus a very small quantity of indicator is added to a system of Acceptor$_1$-Donor$_1$, and an equilibrium such as (II) is realized without the concentrations of the Acceptor$_1$ and Donor$_1$ being affected. The colour of the solution is thus characteristic of the ratio $|\text{Acceptor}_1|/|\text{Donor}_1|$ according to (III).

Notes.—(1) Only one of the two forms of the indicator need be coloured. The coloration then depends on the total concentration of the indicator system (see pH indicators below).

(2) Instead of using changes of colour (coloured indicators) changes in fluorescence (fluorescence indicators) can be used, or the appearance or disappearance of a precipitate (turbidimetric indicators), this latter phenomenon being rendered more easily visible by adsorption of dyes (adsorption indicators), etc.

(3) The indicator system can put several particles into operation. It will then be an indicator for several types of reaction (see later).

pH INDICATORS

Acid-base indicators involve proton exchange.

In aqueous solution, they are in equilibrium with the acid-base system H_3O^+—H_2O and we have

$$I_A + H_2O \rightleftharpoons H_3O^+ + I_B$$

9   115
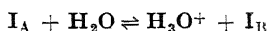
calling the acid form I_A and the basic form I_B. From this

$$\frac{|\,I_B\,|\cdot|\,H_3O^+\,|}{|\,I_A\,|\cdot|\,H_2O\,|} = K$$

whence, using the common simplified form

$$\frac{|\,I_B\,|\cdot|\,H^+\,|}{|\,I_A\,|} = K_A$$

Range of indicators.—If the activity of the H^+ ions increases, the value of $|\,I_B\,|$ will decrease and that of $|\,I_A\,|$ will increase. The addition of H ions causes the basic form to disappear and the acid form to appear: the colour changes and we have

$$pH = pK + \log\frac{|\,I_B\,|}{|\,I_A\,|} \qquad . \quad . \quad . \quad . \quad (I)$$

It may be taken that the coloured acid form predominates when $|\,I_A\,| = 10\,|\,I_B\,|$ and the basic coloured form when $|\,I_B\,| = 10\,|\,I_A\,|$. The indicator changes completely from the basic to the acid colour when the ratio $|\,I_A\,|/|\,I_B\,|$ changes from $1/10$ to 10 or according to (I) when the pH varies from $pK - 1$ to $pK + 1$.

A visible change from one colour to the other requires a certain pH interval, the magnitude of which is in general about 2 units.

Single-colour indicators.—In certain indicator systems, only one of the two forms is coloured. We have, as before:

$$pH = pK + \log\frac{|\,I_B\,|}{|\,I_A\,|}$$

Let the coloured form be I_B and suppose that its colour becomes perceptible when its concentration attains the value c, and let a be the total concentration of the indicator added to the solution. The pH at which the colour appears will be given by

$$pH = pK + \log\frac{c}{a - c}$$

The pH at which the colour appears depends upon a, and thus on the quantity of indicator used.

The dyes which are used as indicators are in general only very slightly soluble in water. A pH for colour change in saturated solution can thus be defined for single-coloured indicators. Thus, phenolphthalein in saturated solution gives a pale pink colour above pH 8. In a solution ten times more dilute, the pink colour appears at pH 9·0. With certain more soluble indicators, the concentration must be taken into consideration.

Note.—In the presence of salts, activities and not concentrations ought to be used in the equations. The pH of colour change can then become quite different.

Other acid-base indicators.—Other types of acid-base indicators can be used:

Fluorescence indicators for use in ultraviolet light: they are occasionally useful for the determination of pH in coloured solutions.

Turbidimitric indicators: the acid or basic form precipitates,

Adsorption indicators: the precipitation is made more evident by the adsorption of a dye, which causes the colour to change.

Other types of pH indicators.—We can in principle use all the types of reaction involving exchanges of protons: exchanges of ions and protons, that is to say coloured complexes which are destroyed by changes of pH; exchanges of electrons and protons, that is to say redox systems which are reduced or oxidized as a result of pH changes.

Principle of the determination of pH of a solution in qualitative analysis.—We shall see in quantitative analysis the methods which the chemist has at his disposal for the determination of the pH of a solution.

In qualitative analysis it is usually sufficient to use 'test papers' whose colour, when a little more precision is required, can be compared with that of some standard tints.

pH is also determined by means of coloured indicators. The colour can be compared with a scale of comparison colours for known pH's, i.e. a chart which shows the colour the system would have at known pH's. This is often printed on the cover of the book of test papers.

Test books of universal indicator paper are available, these 'universal' indicators consisting of a mixture of indicators which permit the determination of the pH to within 1–2 units in a single test.

The use of comparison colour scales permits the determination of the pH of a solution with test papers to within 0·1–0·2 unit in the most favourable cases. It should be borne in mind, however, that the information given by pH indicators, which are sufficient for qualitative analysis, are subject to numerous sources of error: the effect of the concentration of the indicator, the temperature, the concentration of salts, etc.

Common pH indicators

Usual name	Concentration %	Colour		pH
		Acid	Alkali	
Thymol blue . . .	0·001 alc.	red	yellow	1·2–2·8
Methyl yellow . . .	,, ,,	,,	,,	2·9–4·0
Methyl orange . . .	0·001 water	,,	yellow-orange	3·1–4·4
Bromophenol blue .	,, ,,	yellow	blue	3·0–4·6
Bromocresol green .	,, alc.	,,	,,	3·8–5·4
Methyl red . . .	0·002 ,,	red	yellow	4·2–6·2
Chlorophenol red .	0·001 ,,	yellow	red	4·8–6·4
Bromophenol red .	,, ,,	,,	,,	5·2–6·8
Bromothymol blue .	,, ,,	,,	blue	6·0–7·6
Phenol red . . .	,, ,,	,,	red	6·4–8·0
Neutral red . . .	,, ,,	red	yellow-brown	6·8–8·0
Cresol red . . .	,, ,,	yellow	red	7·2–8·8
α-naphtholphthalein .	,, ,,	pink	green	7·3–8·7
Thymol blue . . .	,, ,,	yellow	blue	8·0–9·6
Phenolphthalein .	,, ,,	colourless	red	8·0–9·9
Thymol blue . . .	,, ,,	,,	blue	9·3–10·5
Nile blue . . .	0·001 water	blue	red	10·1–11·1

REDOX POTENTIAL INDICATORS

Redox indicators are systems which exchange electrons. Their colour changes with the redox potential of the solution, that is to say the oxidized and reduced forms of the indicator have different colours.

Range of (redox) indicators.—Let I_o be the oxidized and I_r the reduced form of the indicators. We have, in the most simple case:

$$I_o + ne \rightleftharpoons I_r \quad \text{with} \quad E = E_o + \frac{0 \cdot 06}{n} \log \frac{|I_o|}{|I_r|}$$

The same deductions and calculations as for pH indicators can be made here. The majority of redox indicators can be considered as being single-coloured. The colour of the indicator becomes perceptible above a certain concentration c of the coloured form, and this limits the sensitivity of the indicator. Assuming that the coloured form is the oxidized one, we have, calling the total concentration indicator a:

$$E \text{ change} = E_o + \frac{0 \cdot 06}{n} \log \frac{c}{a - c}$$

The change potential of the indicator thus depends upon the total concentration of the indicator a, but as this concentration is always fixed at a given value the potential of the change point is more or less constant (at least within the reliability of visual observation). In general, the potential of the change point is fixed to within 0·03 volt.

Influence of pH.—It is known that for numerous systems, the redox potential depends upon the pH, in particular when the redox system involves H ions. It is necessary therefore to define the change potential for each pH (fig. 32).

Principal redox indicators in acid solution

Name	Concentration of reagent	No. of drops / 100 ml soln.	Colour		E at pH = 1
			Reduced	Oxidized	
Ferrous o-phen-anthroline	0·025M	2	red	pale blue	1·10
Sodium N-phenyl-anthranilate	1 g/1	2	colourless	purple	1·00
Starch iodide paste	1% paste with 0·01M-KI	5 ml paste 3–4 drops of KI	blue	colourless	0·90
Barium diphenyl-amine sulphonate	0·05%	4–5	colourless	purple	0·83
Starch iodide paste	See above	See above	,,	blue	0·60 0·65
Organic dyes (methylene blue, indigo carmine, etc.)					0·10–0·50

Other types of redox indicators.—There are in principle fluorescence and turbidimetric redox indicators.

Coloured complexes destroyed by oxidation or reduction can also be used.
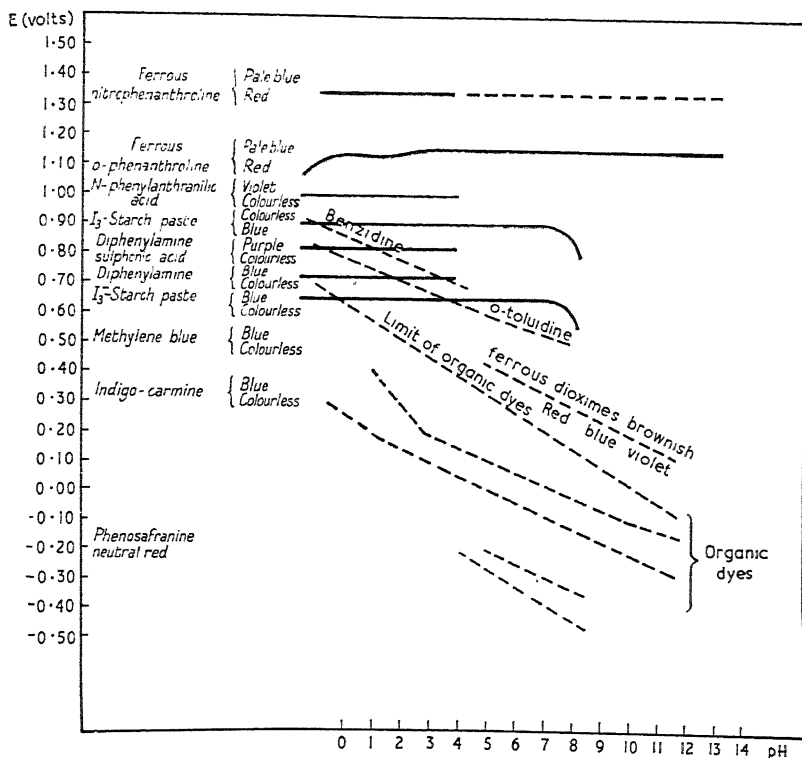
FIG. 32

INDICATORS OF THE CONCENTRATIONS OF IONS

These are systems which involve exchanges of ions. The change of these indicators is caused by changes of the concentrations of the ions in question.

CNS⁻ is an indicator of the concentration of Fe³⁺ ions.—If a given concentration of CNS⁻ is added to a solution containing Fe³⁺, the red coloration of FeCNS²⁺ will be visible above a certain concentration of Fe³⁺.

$$Fe^{3+} + CNS^- \rightleftharpoons FeCNS^{2+}$$

colourless   red
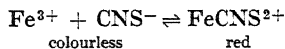
Similar lines of thought apply to these indicators as to pH and redox indicators. We have

$$\frac{|CNS^-| \cdot |Fe^{3+}|}{|FeCNS^{2+}|} = K \quad \text{whence} \quad |Fe^{3+}| = K \cdot \frac{|FeCNS^{2+}|}{|CNS^-|}$$

or

$$\cdot \; pFe^{3+} = pK + \log \frac{|CNS^-|}{|FeCNS^{2+}|}$$

Suppose that the red colour appears when $|\text{FeCNS}^{2+}| = c$. Let a be the total concentration of CNS^- added. We have

$$p\text{Fe}^{3+} = p\text{K} + \log \frac{a - c}{c}$$

The indicator is single-coloured. The appearance of the colour will depend on the total quantity of the indicator CNS^-. For a given a, $p\text{Fe}^{3+}$ is fixed.

There are indicators of various types: fluorescence, turbidimetric, complex, redox, $p\text{H}$, etc.

II. REAGENTS

An indicator of the concentration of an ion is a reagent for that ion. But, whereas the function of the indicator is to determine the concentration of the ion, that of the reagent is only to detect it. The conditions of use of indicators and reagents are therefore different.

CONCENTRATION LIMIT OF REAGENTS.—The concentration limit is the concentration below which the ion sought for can no longer be detected. It is expressed in g.-ion/litre. It is in general 10^{-3}, 10^{-4}, or 10^{-5}. It is often reported in terms of thousandths of a milligram 'γ' per millilitre of solution. This is the same thing as the number of parts per million, or p.p.m.

It is said that a reagent is sensitive when the concentration limit is small, in other words that the reagent is the more sensitive, the lower the concentration of an ion that it can detect.

Examples.—Ferric ions can be detected by thiocyanate ions, with which they give a red coloration. Concentration limit: $4 \cdot 10^{-5}$. The coloration can be concentrated into a small volume by extraction with ether. Limit of sensitivity 10^{-5} g.-ion Fe^{3+} per litre.

The permanganate ion has a very intense red-violet colour. Concentration limit: 10^{-5} g.-ion/litre.

Detection of Ca^{2+} by precipitation of CaC_2O_4: 10^{-3} g.-ion/litre.

Detection of Mg^{2+} as MgNH_4PO_4: 10^{-3} g.-ion/litre.

It is important to have some idea of the sensitivity of different reagents in order to know if traces or considerable quantities of an ion are present. The concentration limit of reagents is in general higher than or equal to 10^{-4} g.-ion/litre. When it is lower, it is a good idea to dilute the solution before test. This precaution avoids the confusion of traces with large quantities. On the other hand, if the sensitivity is not so high, the solution must be concentrated to avoid missing small quantities of the element sought. In this way a better idea of the concentration of different ions in the solution can be gained.

SPECIFICITY.—A reagent is 'specific' for an ion if it does not give the reaction with any other ion. If it reacts with only a small number of ions, it is said to be 'selective'.

DIFFERENT TYPES OF REAGENTS

(1) **Coloured complexes.**—This is the most frequent case.

We know that in order to increase the stability of the complex, and thus the sensitivity of the reaction, certain precautions must be taken:

adjust the *p*H to the region where the complex is as stable as possible and increase the concentration of the complex-forming ion.

In the case of perfect complexes, excess of reagent and variations of *p*H are without influence.

Example.—Detection of ferric ions.—CNS⁻ ions give a red coloration with ferric ions, because of the formation of the complex $FeCNS^{2+}$. It thus detects Fe^{3+}.

The sensitivity of the reaction is greater the larger the CNS⁻ concentration. In practice, to a drop of the solution being examined a drop of saturated thiocyanate (usually ammonium) is added.

Influence of pH.—HCNS is a strong acid, so that variation of *p*H has no influence. $Fe(OH)_3$ is of low solubility and its formation causes the complex to be destroyed. The reaction is therefore carried out in strongly acid solution.

Interfering ions.—(a) Formation of complexes.—Those ions, such as F⁻, which form complexes with Fe^{3+}, diminish the sensitivity or inhibit the reaction by decreasing the free $| Fe^{3+} |$. Those which form complexes with CNS⁻, for example Hg^{2+}, diminish the sensitivity of the reaction: it is useful therefore to have an excess of reagent. Those which also form coloured complexes, such as Cu^{2+}, interfere.

(b) Redox.—Ions which oxidize CNS⁻, for example HNO_2, make it necessary to use excess of the reagent. Here we get coloured oxidation products which always interfere.

(c) Precipitation.—Ions which precipitate Fe^{3+} interfere with or inhibit the reaction. Those which precipitate CNS⁻ require the use of excess of reagent.

Non-aqueous solvents.—The addition of alcohol or acetone decreases the ionization of the complex, and the reaction becomes more sensitive.

Extraction.—Red $Fe(CNS)_3$ can be extracted and, as a result, it can be concentrated in a small volume or separated from interfering colours by means of alcohols or ether. The sensitivity is increased.

(2) **pH indicators.**—A large number of reactions involve protons. Variation of *p*H is shown up by indicators.

Example.—The reaction

$$S_2O_3{}^{2-} + Hg^{2+} + H_2O \longrightarrow HgS \downarrow + SO_4{}^{2-} + 2H^+$$
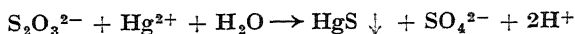
liberates H⁺ ions. As all the other ions present are neutral, the liberation of H⁺ ions decreases the *p*H. Thiosulphates can thus be detected by means of their reaction with Hg^{2+} (mercuric chloride) with the help of a *p*H indicator.

Interfering substances.—Those which can take part in a reaction involving the exchange of H⁺ ions, and in particular, bases such as $CO_3{}^{2-}$: also those which form complexes or precipitate, oxidize or reduce the interacting ions. The arguments are the same as before.

(3) **Redox indicators.**—Redox indicators can be used as reagents for ions in different ways:

(a) Those which change in strongly oxidizing or strongly reducing solutions are very selective.

Example.—Ferrous *o*-phenanthroline, which turns from red to pale blue at 1·1 volts, can only change in the presence of very energetic

oxidants such as MnO_4^-, Ce^{4+}, $V(V)$, etc. Hence these ions can be detected with it.

(b) In particular cases, a redox indicator can become specific for an ion.

(c) In the mixture of $Sn^{2+} + Sb^{3+}$, reduction of ferric dimethyl-glyoxime, with a colour change to red, permits the detection of Sn^{2+}.

Notes.—A large number of reagents can be considered as redox indicators: cacotheline, phosphomolybdic acid, etc. This classification is based entirely on their change potential.

Certain redox indicators are extremely sensitive.

The same remarks can be made here about the influence of pH and of interfering ions, as were made above (p. 121).

(4) **Precipitates.**—The formation of precipitates can be used in order to characterize ions. The reaction is more sensitive when the precipitation is more complete, and when the precipitate is coloured. We know that for this it is necessary to increase the concentration of the precipitating ion. Care must be taken to allow its particles to grow in order to reduce their solubility. The precipitates are affected by pH when they are salts of weak acids or weak bases. Their formation can be inhibited by the formation of complexes.

In general, precipitation reagents are less sensitive than coloration reagents.

Example.—Detection of potassium by sodium cobaltinitrite.—If a precipitate is appreciably soluble (as is potassium cobaltinitrite) care must be taken that its crystals are allowed to form slowly. Sometimes it is necessary to warm the solution. The precipitation can be speeded up by rubbing the sides of the test-tube with a stirrer: in this way vibrations are caused which promote the formation of crystal nuclei.

Interfering ions. Influence of pH (see p. 90)

(5) **Adsorption reagents.**—The formation of a precipitate can be rendered more sensitive and more specific by the adsorption of a dye, which thus changes the colour of the precipitate.

Take for example some of the mixture: magnesium salt–thiazole yellow. The solution is coloured yellow by the dye. In alkaline solution, magnesium hydroxide precipitates and adsorbs the dye, taking on a pink tint. These phenomena of adsorption by the precipitate are frequently utilized (detection of aluminium, beryllium, etc.).

The reaction can be made more sensitive by taking certain precautions. Thus, when looking for magnesium with thiazole yellow, the colour change is sharper if the quantity of dye is such that it can be completely adsorbed by the precipitate. The yellow colour of the solution then disappears completely.

The amount of material adsorbed can be increased by the formation of colloids having very fine particles. There is then no flocculation and it is the solution itself which appears to change colour and not just the precipitate which becomes coloured. These conditions are realized, for example, in the detection of Al^{3+} when precipitating it as the hydroxide in acetate buffer. Put as much dye (aluminon, for example) into the solution as can be tolerated without giving it more than a faint colour (but so also that the amount adsorbed can be as large as possible).

(6) **Fluorescent reagents.**—Certain substances emit visible light when exposed to ultra-violet light. Such types are to be found within the classes of redox, adsorption, complex-forming and precipitating indicators.

Example.—*Detection of sodium.*—Zinc and uranyl acetates are not fluorescent, i.e. they are colourless in U.V. light. Addition of Na^+ ions causes the triple acetate of zinc, uranyl, and sodium to be formed, a slightly soluble compound, which gives a yellow-green fluorescence more perceptible than the mere formation of a precipitate.

Al^{3+} can be detected in the presence of Be^{2+} in U.V. light (p. 158).

(7) **Catalytic methods.**—The catalytic properties of certain ions can be used to detect them.

Example.—Ag^+ increases the rate of oxidation by persulphates. Ferrous-*o*-phenanthroline is oxidized immediately, turning from red to pale blue.

Use of organic reagents.—The use of organic reagents has enabled some important advances to be made in the technique of analysis.

In general, the complexes obtained can be much more stable, and the precipitates much less soluble, than purely inorganic ones. The sensitivity of the colorations is frequently very large.

With certain organic reagents a coloration or precipitate specific to some particular ion is sometimes obtained.

In addition, compounds of inorganic ions with organic reagents can frequently be extracted by organic solvents which are immiscible with water.

Inner complexes.—(1) The properties of organic reagents vis-a-vis inorganic ones can frequently be explained by the formation of co-ordinate bonds with concomitant cyclization ('inner complexes').

Example.—Oxine gives compounds with inorganic ions.
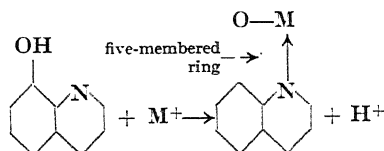
The most important groups which display this facility for forming co-ordinate bonds by the donation of an electron pair are: $\equiv N$, $=O$, $=S$.

2 hydroxyl groups in a benzenoid or other ring, in the ortho position to one another, permit the formation of a five-membered ring.

1 OH and 1 CO_2H, ortho to one another, can produce a six-membered ring.

1 OH and 1 (—N=N—) group, ortho to one another, can produce a six-membered ring.
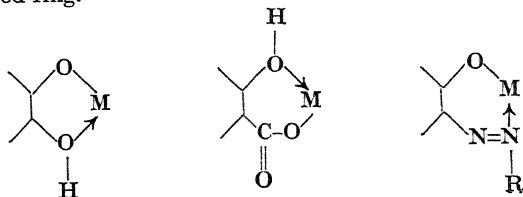
The interaction between atoms, represented formally by a co-ordinate bond, is in general sufficiently weak that all the deductions we have made about salts are applicable to inner complexes.

(2) When inner complexes are formed between organic reagents and inorganic ions, the colour generally changes from yellow to red, then to blue or green, and finally to black.

SOME REMARKS ON THE RELATIONS BETWEEN THE PROPERTIES OF IONS IN SOLUTION AND THEIR ELECTRONIC STRUCTURE

UP till now we have tried to predict reactions mainly from experimentally determined data about various systems (acid-base, redox, etc.), as expressed in such constants as the redox potentials and the equilibrium constants. From these constants it is possible, at any rate in theory, to predict all possible equilibria in the systems. But to complete the picture, it is necessary, in certain cases, to make some reservations about the rates at which these equilibria are attained.

In all this we have made no reference to any mechanism or to structures. To what extent can the study of the structure of a compound enable one to predict phenomena, in particular the existence of various chemical species in solution and the possible reactions which they may undergo? It must be recognized that so far structural theory has provided few useful results.

Without going into considerations of structures (see the bibliography, p. 131) we have brought together here some rules which enable one to predict qualitatively certain properties.

(I) VARIATION OF PROPERTIES INSIDE THE PERIODIC CLASSIFICATION

The properties of the elements and their compounds vary fairly regularly within the periodic classification, both for the elements of the 'a' columns, and for those of the 'b' columns, as shown below.

a COLUMNS

	I	II	III	IV	V	VI	VII
1	Li	Be	B	C			
2	Na	Mg	Al	Si			
3	K	Ca	Sc	Ti	V	Cr	Mn
4	Rb	Sr	Y	Zr	Nb	Mo	Tc
5	Cs	Ba	R.E.	Hf	Ta	W	Re
				Th		U	
6	Fa	Ra	Ac		Pa		

b COLUMNS

→

	I	II	III	IV	V	VI	VII
1				C	N	O	F
2				Si	P	S	Cl
3	Cu	Zn	Ga	Ge	As	Se	Br
4	Ag	Cd	In	Sn	Sb	Te	I
5	Au	Hg	Tl	Pb	Bi	Po	At

Influence of radius and charge of an ion on its acid-basic properties.—In a polar solvent like water the ions are solvated. Consider two cations Na^+ and Cl^{7+} which are both to be found on the second row of the classification. As a result of the charge carried by Cl^{7+} the ionic radius is smaller and so the attraction for water molecules is larger. This attraction is also reinforced by increase of the charge; the deformation of a polar molecule of water will be greater, H^+ will be separated more easily. In effect the acid (Cl^{7+}, mH_2O) is stronger. It can be said that Cl^{7+} binds O^{2-} more firmly and that the bond between them is less electrovalent; as a result the bond between O^{2-} and H^+ is weaker and more electrovalent. It is thus in large measure the radius and charge of the ion which determines certain of its properties. In both sub-groups of the classification the ionic radius decreases from the bottom to the top and from left to right and the charges increase from left to right.

Precipitation of hydroxides.—If the hydroxide is of low solubility the acid strength of the cation will be apparently reinforced and the acid strength of the hydroxide will be apparently decreased by this fact. The hydroxides are in general less soluble as their molecular weight increases, in particular from the top to the bottom of the classification. This influence in effect runs counter to the preceding one in the columns of the periodic classification. In spite of this some approximate rules can be formulated and are given later on.

The hydroxides of elements towards the top and to the right of the classification have an appreciable solubility. They are dealt with separately in the classification above.

We are concerned here with the existence of molecules in solution. Thus $Ca(OH)_2$ is of low solubility in sufficiently alkaline solution, such as NaOH.

The strength of the acid-base pair and the periodic classification.—The strength of the acid-base pair is a fundamental property which determines the region of existence of ions. This property varies regularly with the place of the elements in the periodic table. The inexactness of many of the values prevents us from giving a complete table.

Elements of the a *columns*

(1) Along a given row of the classification the cations increase in acidity from left to right. The basicity of the hydroxides thus decreases, and their acid strength almost always also increases in the same direction. The corresponding anions decrease in basicity in the same direction.

The pK value varies from $+ \infty$ to $- \infty$ from left to right.

For a given column the same rule applies frequently, from the bottom to the top.

More acid

$\longrightarrow$

Li^+	Be^{2+}	B^{3+}	C^{4+}
Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
K^+	Ca^{2+}		

(More acid, upward)

Note.—Two compounds located respectively to the right and below a given element can thus have similar properties. For example, Li^+ and Mg^{2+} are both more acid than Na^+; Be(II) and Al(III), B(III) and Si(IV) are similar.

Examples.—Starting with aluminium, the domain of existence of its ions is shown schematically below:

$$Al^{3+} \qquad Al(OH)_3 \downarrow \qquad AlO_2^-$$

pH 4   11

With boron the cation and the hydroxide are more acid.

$$B^{3+} \qquad\qquad HBO_2 \qquad\qquad BO_2^-$$

The same happens with silicon which thus resembles boron.

$$Si^{4+} \qquad H_2SiO_3 \downarrow \qquad HSiO_3^- \qquad SiO_3^{2-}$$

Cations for these two elements do not exist since they are too acid; but the anions are more important than those of aluminium.

In magnesium the properties are displaced in the reverse direction:

$$Mg^{2+} \qquad\qquad Mg(OH)_2 \downarrow$$

11

The cation exists over a large range of pH while the anion does not.

With sodium there is a further displacement in the same direction, so that only cations are present in the solution whatever the pH.

$$Na^+ \qquad\qquad NaOH$$

As a result the hydroxides are very strong bases at the bottom and left-hand corner of the periodic classification; only cations are present in solution. On the other hand, in the right-hand top corner the hydroxides are strong acids, completely ionized, and only the anions such as MnO_4^-, etc., are present.

Elements of the b columns.—Same rules:

More acid

$\longrightarrow$

Cu^+	Zn^{2+}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}
Ag^+	Cd^{2+}				
Au^+	Hg^{2+}				

(More acid, upward)

Exceptions.—Tl^{3+} is more acid than Ga^{3+} and In^{3+}; Hg^{2+} than Cd^{2+}, Au^+ than Ag^+.

Negative oxidation states

IV	V	VI	VII
C^{4-}	N^{3-}	O^{2-}	F^-
Si^{4-}	P^{3-}	S^{2-}	Cl^-
Ce^{4-}	As^{3-}	Se^{2-}	Br^-
Sn^{4-}	Sb^{3-}	Te^{2-}	I^-
		Po^{2-}	

The ionic radius increases from O^{2-} to S^{2-}, thus H^+ is less and less firmly bound, so that the corresponding acids are stronger and stronger. They increase in strength in the direction of the arrows.

General properties

(a) In the same column the elements of the fourth and fifth lines are in general very similar: Rb—Cs; Sr—Ba; Y—rare earths; Zr—Hf; Nb—Ta; Mo—W; Tc—Re; Ru—Os; Rh—Ir; Pd—Pt.
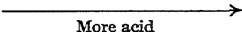
The elements of the sixth rows are in general fairly different. Above the fourth row the differences become more and more marked. Between the first and second row the differences are large.

The analogies between neighbouring elements in the same line are marked but much smaller.

The same remarks as those above apply. The analogies are here particularly strongly marked between Cu^I—Ag; Zn—Cd; Ga—In; Ge—Sn; As—Sb; Se—Te; Br—I.

Note.—Analogous rules apply to the different oxidation states. Thus we are justified in comparing:

II+	III+	IV+	V+
C	N		
Si	P	S	Cl
Ge	As	Se	Br
Sn	Sb	Te	I
Pb	Bi	Po	At

More acid →

VARIATIONS OF PROPERTIES WITH STATE OF OXIDATION

For a given element, as the degree of oxidation increases the ionic radius decreases. The charge increases and so the corresponding cations are more and more acid.

Cations.—(1) When the state of oxidation increases the cation becomes more and more acid, the corresponding hydroxide becomes less and less basic and the pK decreases.

Example.—(*a*) Chlorine derivatives:

<div align="center">More acid →</div>

$$Cl^+ \qquad Cl^{3+} \qquad Cl^{5+} \qquad Cl^{7+}$$
$$HClO \qquad HClO_2 \qquad HClO_3 \qquad HClO_4$$

<div align="center">← More basic</div>
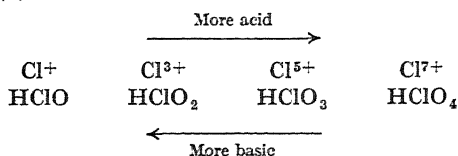
(*b*) Cations derived from chromium:

<div align="center">More acid →</div>

$$Cr^{2+} \qquad\qquad Cr^{3+} \qquad\qquad Cr^{6+}$$
$$Cr(OH)_2 \downarrow \qquad Cr(OH)_3 \downarrow \qquad H_2CrO_4$$

<div align="center">← More basic</div>
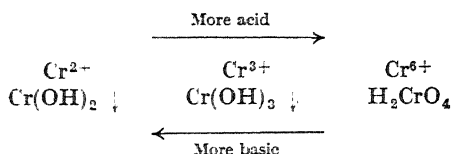
(2) It can also be said that the hydroxide itself frequently becomes more acid when its oxidation number increases.

HClO ClO$^-$	HClO$_2$ ClO$_2^-$	HClO$_3$ ClO$_3^-$	HClO$_4$ ClO$_4^-$
*p*K:　7·6	4·0	strong	very strong
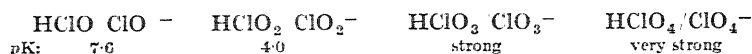
Nitric acid, $HNO_3(N(V))$, is a strong acid. Nitrous acid $HNO_2(N(III))$ is weak: $pK = 3·4$.

Sulphurous acid (S(IV)) has the following constants: $pk_2 = 1·8$, $pk_1 = 5·3$. Sulphuric acid (S(VI)) is strong in its first dissociation and fairly strong in its second: $pk_1 = 1·9$. Persulphuric acid $H_2S_2O_8(S(VII))$ is strong in both dissociations. The hydroxides, when they precipitate, reinforce the strength of the cation as an acid, which acts in the same direction as the preceding influences (there are some exceptions: $Cu^{2+} - Cu^+$), but the strength of the hydroxide as an acid is decreased, which acts in the opposite direction.

However, the preceding rule can often be applied.

We know that the more acid the cation the more narrow its range of existence. Increase of the state of oxidation, which increases the strength of the acid, reduces the region of existence of the cations to very acid solutions. In the higher state of oxidation, the anion in general exists, the corresponding hydroxide being a strong acid.

Example.—The domain of existence of manganese ions

	Mn^{2+}	Mn(OH)$_2 \downarrow$	
2$^+$	——│—————————————	—│——	
	0	14	
	Mn^{3+}　　Mn(OH)$_3 \downarrow$		
3$^-$	——————————	——————	
	Mn(OH)$_4 \downarrow$	Na$_2$MnO$_3$	
4$^+$	—————————		
		disproportionation	MnO$_4{}^{3-}$
5$^+$	—— ———————	——————————|———	
	disproportionation	MnO$_4{}^{2-}$	
6$^+$	—————————	———	
	MnO$_4{}^-$		
7$^+$	——————	————————	
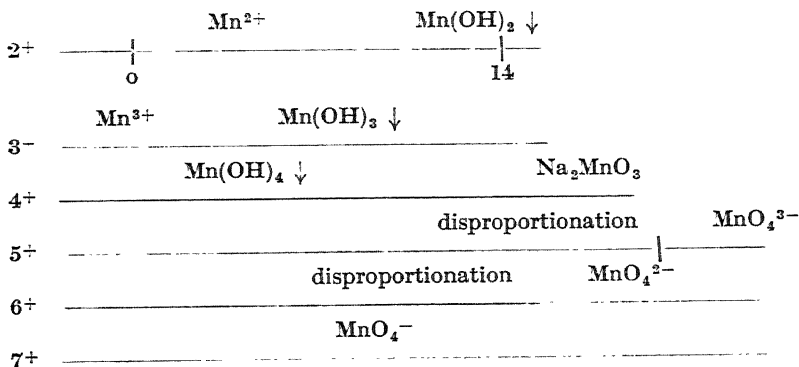
Stability of complexes.—Similar remarks can be made about complexes, although their application is very limited in view of the complexity of the phenomena.

Thus the complexes of Co^{3+} are more stable than the corresponding ones of Co^{2+}, whenever precipitation, proton exchange, or redox do not interfere. The same can be said about complexes of Fe^{3+} compared with those of Fe^{2+}.

The sulphide complexes of Sn^{4+} are more stable than those of Sn^{2+}, etc.

The complex acids are in general stronger, the more stable the complex, and the complex acid is stronger than the simple acid corresponding: $H_3(Fe(CN)_6)$ and HCN, H_2SiF_6 and HF, etc.

Rates of redox reactions.—See the rule, page 111.

Metals and non-metals.—These two classifications describe more a function than an assemblage of properties: an element can behave sometimes as a metal and sometimes as a non-metal. The elements can be classified according to their properties and those of their ions, either as acids-bases, or as oxidants and reductants. The two classifications coincide in so far as these two kinds of properties are parallel.

(1) *As acid-bases.*—The name 'metal' is frequently given to elements which give cations more easily and the name 'non-metal' to those which give anions. The metals are thus at the bottom and the left of the classification and the non-metals at the top and the right.

(2) *As oxidants and reductants.*—The name metal can also be applied to the elements which are easily oxidized and that of non-metal to those which are easily reduced.

Metals.—All elements are capable of being oxidized in solution in water with the exception of fluorine.

$$Na \downarrow - e \longrightarrow Na^+ \qquad I^0 - e + HO^- \longrightarrow HIO$$
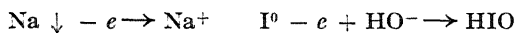
The more metallic elements are those which are more easy to oxidize. These are the alkalis and the alkaline earths. The less easily oxidized metals: gold, platinum, mercury, silver, are called 'noble' metals. Hydrogen is a metal in the reaction:

$$H_2 \uparrow - 2e \longrightarrow 2H^+$$
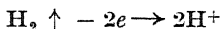
Non-metals.—These are the reducible elements:

$$As \downarrow - 3e + 3H^+ \longrightarrow AsH_3 \uparrow$$
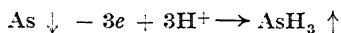
In the periodic classification they appear as follows:

B^{3-}	C^{4-}	N^{3-}	O^{2-} . . $+ 0.16$ volt	F^- . . . 2.85 volts
	Si^{4-}	P^{3-}	S^{2-} . . $- 0.50$,,	Cl^- . . . 1.41 ,,
	Ge^{4-}	As^{3-}	Se^{2-} . . $- 0.77$,,	Br^- . . . 1.09 ,,
		Sb^{3-}	Te^{2-} . . $- 0.9$,,	I^- . . . 0.62 volt
			Po^{2-} . . $- 1.00$,,	

The easiest to reduce is fluorine, which has the most strongly marked non-metallic character. The majority of elements cannot be reduced in aqueous solution. They give ions which are too strongly reducing. Hydrogen is a non-metal in the H^- ion, an extremely strong reductant, not stable in water. The rare gases are neither metals nor non-metals.

Some elements are frequently both oxidizable and reducible: sulphur, selenium, tellurium, polonium, chlorine, bromine, iodine, arsenic, antimony, etc.

Thus iodine is fairly noble as a metal. $I^0/I^+ = 1 \cdot 00$ volt, and as a non-metal we have $I^0/I^- = 0 \cdot 60$ volt.

These elements can disproportionate and thus behave at one and the same time as metals and non-metals:

$$4S \downarrow + 6OH^- \longrightarrow S_2O_3{}^{2-} + 2S^{2-} + 3H_2O$$
$$Cl_2 + OH^- \longrightarrow HClO + Cl^-$$
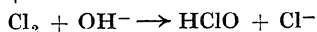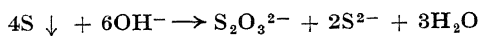
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PART II

CHEMICAL PROPERTIES AND THE CHARACTERIZATION OF IONS

INTRODUCTION

THE properties of ions in aqueous solution are defined by a knowledge of the following parameters:

(1) The strength of acid-base pairs.

(2) The list of compounds which are only slightly ionized (low solubility and complex) with their equilibrium constants: solubility products or stability constants;

(3) The formal redox potentials of the redox systems as a function of pH.

This should be extended by information about the rates of these reactions and the catalysts which accelerate them.

We shall strive to give these properties for each state of oxidation of each element.

INSTRUCTIONS FOR THE USE OF THE TABLES AND CURVES

(1) **Solubility curve for the hydroxide as a function of pH.**— These curves were discussed in the chapter on precipitation. We should emphasize here once again that these curves, as well as the corresponding precipitation pH's, are only first approximations to descriptions of the phenomena. Basic and condensed ions, the ageing of the precipitate, the influence of temperature, the formation of complexes, chloride or sulphate ones for example, can cause predictions to be modified.

Example.—The solubility curve for aluminium hydroxide facilitates the prediction, in a more direct fashion than the solubility product, of the effect of different reagents on a solution of an aluminium salt. This was referred to on page 77.

(2) **Tables of slightly ionized compounds and reagents.**—These tables contain, in particular, all the important compounds which can affect the precipitation of the hydroxide.

The values of the equilibrium constants which are given permit the prediction of reactions from simple calculations.

Our actual knowledge about the formulae and the stabilities of the compounds in solution is unfortunately very limited.

Conventions.—The tables give the negative logarithms (to base 10) of the constants. The ionic strength I and the temperature are shown wherever possible.

Thus

$$Ag(CH_3COO) \rightleftharpoons Ag^+ + CH_3COO^- \ldots 0.7$$
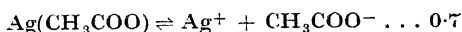
means that

$$\frac{|\,Ag^+\,|\cdot|\,CH_3COO^-\,|}{|\,Ag(CH_3COO)\,|} = 10^{-0.7}$$

The sign $\downarrow$ indicates that the substance thus characterized is a solid

in presence of the solution: the activity corresponding to it is always taken equal to unity. Thus

$$AgCH_3COO \downarrow \rightleftharpoons Ag^+ + CH_3COO^- \ldots 2 \cdot 7$$
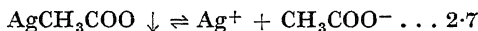
means that we have

$$| Ag^+ | \cdot | CH_3COO^- | = 10^{-2 \cdot 7}$$

The sign $\uparrow$ indicates that the substance so characterized is a gas at atmospheric pressure in the presence of the solution, the activity corresponding to this is also always taken as unity. Thus

$$CO_2 \uparrow + H_2O = HCO_3^- + H^+ \ldots 7 \cdot 8$$

means that $\quad\quad | HCO_3^- | \cdot | H^+ | = 10^{-7 \cdot 8}$

If the pressure of CO_2 (the partial pressure for example) is different from that of the atmosphere, we then have

$$\frac{| HCO_3^- | \cdot | H^+ |}{p_{CO_2}} = 10^{-7 \cdot 8}$$

where p_{CO_2} is the pressure of the CO_2 above the solution in atmospheres.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \ldots 6 \cdot 4$$

means that

$$\frac{| HCO_3^- | \cdot | H^+ |}{| CO_2 |} \rightleftharpoons 10^{-6 \cdot 4}$$

When there are several successive complexes, the partial equilibria are represented by pk_1, pk_2, pk_3, etc., and the overall equilibria by pK_1, pK_2, pK_3, etc. Thus, for the argentoammine complexes:

$$pk_2 = 3 \cdot 8 \text{ if } \frac{| AgNH_3^+ | \cdot | NH_3 |}{| Ag(NH_3)_2^+ |} = 10^{-3 \cdot 8}$$

$$pK_2 = 7 \cdot 0 \text{ if } \frac{| Ag^+ | \cdot | NH_3 |^2}{| Ag(NH_3)_2^+ |} = 10^{-7 \cdot 0}$$

Priming of the k's or K's (= k' or K') indicates that the constant given is a formal one valid only for the conditions given, for instance at a given ionic strength when concentrations are used instead of activities.

Application.—Slightly ionized compounds of silver.—(For a more complete table, see p. 243.)

$$
\begin{array}{lr}
Ag_2SO_4 \downarrow \rightleftharpoons 2Ag^+ + SO_4{}^{2-} \ldots \ldots \ldots & 4 \cdot 2 \\
Ag_2CrO_4 \downarrow \rightleftharpoons 2Ag^+ + CrO_4{}^{2-} \ldots \ldots \ldots & 11 \cdot 4 \\
AgIO_3 \downarrow \rightleftharpoons Ag^+ + IO_3^- \ldots \ldots \ldots & 7 \cdot 3 \\
Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 \ldots \ldots \ldots & 7 \cdot 0 \\
AgCl \downarrow \rightleftharpoons Ag^+ + Cl^- \ldots \ldots \ldots & 9 \cdot 7 \\
AgBr \downarrow \rightleftharpoons Ag^+ + Br^- \ldots \ldots \ldots & 12 \cdot 3 \\
AgI \downarrow \rightleftharpoons Ag^+ + I^- \ldots \ldots \ldots & 16 \cdot 0 \\
Ag(S_2O_3)_3{}^{5-} \rightleftharpoons Ag^+ + 3S_2O_3{}^{2-} \ldots \ldots \ldots & 1 \cdot 30 \\
Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^- \ldots \ldots \ldots & 20 \cdot 9 \\
Ag_2S \downarrow \rightleftharpoons 2Ag^+ + S^{2-} \ldots \ldots \ldots & 50
\end{array}
$$

Notes.—(1) The relation given for Ag_2SO_4 means that

$$| Ag^+ |^2 \cdot | SO_4{}^{2-} | = 10^{-4 \cdot 2}$$

Consequently, if the free $| SO_4{}^{2-} | = 10^{-1}$, then the free $| Ag^+ | = 10^{-1 \cdot 6}$.

The relation for $Ag(NH_3)_2{}^+$ means that

$$\frac{|\ Ag^+\ | \cdot |\ NH_3\ |^2}{|\ Ag(NH_3)_2{}^+\ |} = 10^{-7\cdot 0}$$

For $|\ Ag(NH_3)_2{}^+\ | = 10^{-2}$ and $|\ NH_3\ | = 10^{-1}$, $|\ Ag^+\ | = 10^{-7\cdot 0}$

(2) Silver sulphide is the least soluble. The addition of an alkali sulphide to precipitates of other salts transforms them into the black sulphide.

(3) Ammonia dissolves many precipitates. Thus $AgIO_3$, Ag_2CrO_4, Ag_2SO_4 are soluble in $0\cdot1M$-NH_3.

If the concentration of NH_3 is increased, and if an excess of the precipitating ion is not added, AgCl dissolves, AgBr does so with difficulty, whilst AgI scarcely dissolves at all as a simple calculation shows (see p. 87).

Thiosulphate and cyanide ions dissolve all the precipitates, except the sulphide.

(4) The salts of weak acids are more soluble in acid solution; AgI, AgBr, AgCl, $AgIO_3$, AgCNS, $AgBrO_3$ being salts of strong acids have only a small solubility in nitric acid; on the other hand, Ag_3AsO_4, Ag_3PO_4, Ag_2CO_3, etc., dissolve in this acid. Ag_2S has a much enhanced solubility in acid solution, but, in spite of this, very little dissolves on account of its low initial solubility (see p. 80).

(5) The stability of the complexes is a function of the pH. Thus, the complex with NH_3 is destroyed in acid solution. The cyanide complex remains stable under these conditions, although CN^- is a fairly strong base, because the stability of the complex is so very high.

(6) The oxidation potential decreases in going down the table. While it is easy to reduce silver sulphate (E $= 0\cdot72$ volt) it is more difficult to reduce silver iodide ($0\cdot33$ volt) or the cyanide complex.

(7) When foreign ions are present, activities must be used (see p. 11).

(8) Redox diagrams.—The apparent potential of redox systems as a function of pH is given, so that by superimposing the various graphs the oxidation reactions which occur in all these media can be predicted.

In relation to these also, reservations must be made about the effects of temperature, the formation of complexes, precipitation, the fact that reactions may be extremely slow, and about the presence of catalysts. It will be remembered that for these reactions to be quantitative the difference of potential between the two systems must be $0\cdot15$–$0\cdot35$ volt.

Wherever possible, we have given as an approximate indication the value of the oxidation or reduction potential, either for electrochemical, or for chemical, reaction (see p. 108).

ALKALI GROUP

GENERAL CHARACTERISTICS

THE alkali group includes the elements of group Ia of the periodic table: lithium, sodium, potassium, rubidium, and caesium. This is a fairly homogeneous group; K^+, Rb^+, Cs^+ are very similar; Na^+ is slightly different; Li^+ marks the transition between Na^+ and Ca^{2+}. The ammonium ion NH_4^+ is similar to K^+.

Ia	IIa
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fa	Ra

State of oxidation.—Only I$^+$.

Redox.—$E = E_0 + 0.06 \log | M^+ |$. This E_0 is of the order of $- 2.7$ to $- 3.0$ volts. The metals are extremely strong reductants and reduce practically all compounds. In water, hydrogen ions are reduced, even in alkaline solution.

$$2Na \downarrow + 2H^+ \longrightarrow 2Na^+ + H_2 \uparrow$$
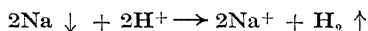
The salts cannot be reduced in solution, except by electrolysis.

Hydroxides.—These are strong bases (apart from ammonia): KOH is slightly stronger than NaOH; in concentrated solution, it is more strongly ionized.

They are all very soluble.

The cations are colourless.

There are no anions.

There are practically no complexes: KSO_4^-, $NaSO_4^-$ are very unstable, and Na_2O_2, a complex with O_2^-, is not very stable.
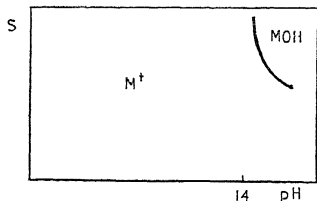
FIG. 33.—APPARENT SOLUBILITY OF THE ALKALI HYDROXIDES AS A FUNCTION OF pH

The alkali ions are difficult to characterize because they do not form complexes, compounds of low solubility, or partake in redox reactions.

POTASSIUM

K = 39·10

K^+.—Solubility of less soluble compounds.

$KBrO_3$	0·4M	$K_2[PtCl_6]$	0·016M
$KClO_3$	0·6M	KIO_4	0·03M
KIO_3	0·4M	Bitartrate	0·04M
$KMnO_4$	0·4M	Picrate	0·02M
$K_2S_2O_8$	0·2M	$K_2(SiF_6)$	0·006M
$KClO_4$	0·15M	$K_2Na[Co(NO_2)_6]$ . .	$\sim$ 0·001M

Detection.—(1) **Cobaltinitrite.**—A concentrated solution of sodium cobaltinitrite produces a yellow precipitate of composition

$$K_2Na(Co(NO_2)_6),H_2O$$
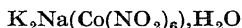
Solution required

Sodium cobaltinitrite	20 g
Sodium acetate	20 g
Acetic acid	20 ml
Water	80 ml

It is destroyed very slowly giving Co^{2+}.

Procedure.—In a microcone place a drop of the solution under test and a drop of the reagent. Wait. The solution ought to be slightly acid, neutral, or slightly alkaline on account of the stability of the cobalti-nitrite complex.

Concentration limit.—$5 . 10^{-4}$ g.-ion of K^+ per litre, or 20 p.p.m.

Interfering ions.—(1) If the acidity is too high, the compound is destroyed, because NO_2^- is a base, $pK = 3·2$. If the acidity is too low, $Co(OH)_3$ precipitates. Hence the solution needs buffering with an acetate buffer.

(2) Powerful oxidants destroy the compound by oxidation of NO_2^-. Powerful reductants reduce Co^{3+} and NO_2^{2-}. An excess of re-agent is therefore necessary. The reagent itself is destroyed slowly by reduction of the Co^{3+} by the NO_2^-. It cannot be kept for more than a few weeks.

(3) Ions which form complexes with Co^{3+}, like CN^-, make the addition of an excess of reagent necessary.

(4) NH_4^+, Cs^+, Rb^+, give the same reaction. NH_4^+ can be elimin-ated by prior boiling of the solution with 4N caustic soda (three drops for one drop of solution).

Small amounts of alkaline earths and of magnesium do not inter-fere. Potassium can be detected in the presence of about 1500 times as much sodium.

UO_2^{2+}, Sb(III), Bi(III), Sn(IV) precipitate, as also does VO_2^+. They must be separated (see later on). Al^{3+}, Cu^{2+}, Co^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Fe^{3+}, Cd^{2+}, Ti(IV), Mo(VI), W(VI), V(V), As(III) and As(V) do not interfere. Nor does H_3PO_4.

(2) **Other low-solubility compounds of potassium sometimes utilized in its detection.**—**Hexanitrodiphenylamine or dipicryl-amine.**—The compound with K^+ is soluble in the majority of alcohols, esters, and ethers. It can thus be extracted from aqueous solution.

Potassium platinichloride, not very soluble in alcohol. NH_4^+, Cs^+, Rb^+, give the same reaction.

(3) **Visible spectrum.**—Red lines at 766–770 mμ. Violet line at 404 mμ.

Flame colour.—Violet.

AMMONIUM

NH_4^+.—The solubilities of its salts are close to those of K^+.

Ammonia.—Ammonia is present in solution almost entirely as NH_4OH.

$$NH_4OH \rightleftharpoons NH_3 + H_2O \ldots 1.7$$
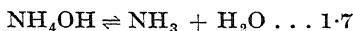
and also $\qquad NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \ldots 9.2$

Unlike the other ions of the alkali metals, which are neutral, NH_4^+ is slightly acid.

Solubilities of salts

NH_4ClO_4 . . . . . 2.0M	$(NH_4)_2(PtCl_6)$	0.01NH_4^+ per litre
NH_4IO_4 . . . . . 0.13M	$(NH_4)_2Na[Co(NO_2)_6]$	. 0.001M
Bitartrate 0.13M		

Complexes.—There are no known complexes with NH_4^+. There are a number of complexes with NH_3 which are destroyed by acids and which are stabilized by ammonium salts. (See complexes with ammonia, p. 48.)

Redox.—NH_4^+ is oxidized in acid solution by aqua regia, chlorine, bromine, etc., and in alkaline solution by hypochlorites, hypobromites, permanganate, and persulphate in the presence of Ag^+ ions (see p. 294).

Nitrates and nitrites are reduced in strongly alkaline solution by powerful reductants like zinc and aluminium, giving ammonia (p. 294), in acid solution by Cr^{2+}, V^{2+}, giving NH_4^+.

Salts.—These are volatile below 1000° C., except those of the relatively non-volatile acids, such as phosphate, borate, and sulphate.

Detection.—Liberation of ammonia.—Nessler reagent.—By heating in alkaline solution, ammonia is liberated and, in the presence of Nessler reagent, gives an orange colour or precipitate.

Solutions required.— (*a*) 4N-NaOH.

(*b*) Nessler reagent.

Potassium iodide	. . . .	3.5 g
Mercuric chloride	. . . .	1.3 g
Water . .	. . . .	70 ml
Caustic soda (4N)	. . . .	30 ml

Procedure.—Into a test-tube place a drop of the solution under test and 3 drops of 4N-NaOH. Bring a stirring rod wetted with the reagent near to the solution (fig. 92 (*b*), p. 326). Heat on a water bath.

Concentration limit.—$5 \cdot 10^{-5}$ g.-ion/litre, or 1 p.p.m.

Interfering ions.—The reaction is specific

Remarks about precipitation by caustic soda.—The addition of caustic soda in excess precipitates the following hydroxides: Bi(III) white, turning yellow when warmed; Cd(II) white; Ce(III) white, turning yellow in air; rare earths; Cr(III) green solution giving a grey precipitate on boiling; Co(II) blue, turning pink on heating; Cu(II) blue, turning black on heating; Fe(II) green, turning rust; Fe(III) rust; In(III) white; Mg(II)

white; Mn(II) white, going brown in air; Hg(II) yellow; Ni(II) green; Tl(III) rust; Th(IV) white; Ti(IV) white; Zr(IV) white.

The precious metals give coloured precipitates.

The white hydroxides of Be(II) and Sn(IV) can be precipitated by boiling.

Phosphates and arsenates can precipitate.

None of these precipitations is sensitive (10^{-2} to 10^{-3} g.-ion/litre). Hence the absence of a precipitate only indicates the absence of considerable quantities of these elements.

SODIUM

$$Na = 23 \cdot 00$$

Low-solubility compounds

Na_2SiF_6	0·03M
$3UO_2(CH_3CO_2)_2$, $Zn(CH_3CO_2)_2$, $Na(CH_3CO_2)$, $6H_2O$ . . .	0·02M
$NaSbO_3$, $3H_2O$	0·016M

Detection.—Zinc uranyl acetate.—Zinc uranyl acetate gives in neutral or slightly acid solution a precipitate of the triple acetate of uranyl, zinc, and sodium, yellowish crystals. At the same time a precipitate of the double acetate of uranyl and sodium, tetrahedra, having the same colour, comes down. Examine under the microscope.

With magnesium instead of zinc, a triple acetate similar to the preceding one is obtained, but its crystals are paler.

Concentration limit.—0·03 g.-ion of Na^+ per litre or 700 p.p.m.

The reaction can be performed on a microscope slide and the crystals obtained examined under a microscope. $10^{-4·6}$ g.-ion/litre can then be detected.

The compound which is formed is fluorescent, in contrast to the reagent itself which is only slightly fluorescent; hence the reaction can be carried out, or the results of it examined, in U.V. light. In this way the presence of 0·001M-Na in solution can be detected with great certainty.

Solution required

Uranyl acetate	10 g
Zinc acetate	10 g
Acetic acid	15 ml
Water	80 ml

Procedure.—Take a strip of hard filter paper 3–4 mm long and place a drop of solution on its end. Dry above a small flame. Place a drop of reagent on the same point, so as to wet a slightly larger surface. Observe in U.V. light the fluorescence which occurs when sodium is present.

Make a blank test.

Concentration limit.—10^{-3} g.-ion/litre (depending on the source of U.V. light employed) = 20 p.p.m.

Interfering substances.—(1) If the acidity is too high, the compound is soluble because CH_3COO^- is a base. If the acidity of the solution is

too low, uranium precipitates (as a uranate). Hence the use of an acetate buffer.

(2) Normal reductants do not reduce UO_2^{2+}.

(3) Ions which produce complexes with UO_2^{2+} or Zn^{2+} do not interfere, if an excess of reagent is used.

(4) Not many ions give precipitates like that of Na^+. K^+ gives a crystalline precipitate when its concentration exceeds $0.1M$; the fluorescence of this precipitate is much weaker than that of the sodium compound. To effect a separation, the potassium is precipitated as perchlorate by addition of perchloric acid, and the precipitate is centrifuged out. Li^+ interferes if its concentration is greater than $0.1M$ (slightly fluorescent).

Ba^{2+} gives a slight turbidity when its concentration exceeds $0.1M$, but no fluorescence. If it is desired to separate it, ammonium sulphate is added to the solution until the precipitation of barium sulphate just ceases. This precipitate is then filtered off, and the solution concentrated back to its initial volume.

Ca^{2+} in high concentration gives a fluorescent precipitate, and so does Be^{2+}. Zn^{2+}, Ce^{3+}, NH_4^+, Fe^{3+}, Fe^{2+}, Al^{3+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Sn^{4+}, Sn^{2+}, As^{3+}, Tl^+, Th^{4+}, Zr^{4+}, Sr^{2+}, Mg^{2+}, Cd^{2+}, V^{5+}, Ce^{4+}, Hg^{2+}, Pb^{2+} do not interfere. $Ti(IV)$, $Sb(III)$, $Bi(III)$ precipitate.

H_3PO_4 and H_3AsO_4 as well as $Mo(VI)$ precipitate the uranium in the reagent. They can be separated by heating for 2–3 minutes on a water bath in the presence of $ZnCO_3$. Centrifuge out the precipitate.

The other ions which interfere can be separated by a preliminary treatment with phosphate.

Detection of Na^+ and K^+ in the initial solution.—If they interfere, foreign ions must be separated. To do this, evaporate the solution to dryness on the water bath in the presence of conc. HCl, if this has not already been done. Redissolve in hot water. Separate.

Add to the solution an excess of lead acetate. Warm. Separate. Add an excess of diammonium phosphate so as to bring its concentration in the solution up to 15 (wt.) per cent. Boil. Cool. Separate. Concentrate and divide into two parts. Treat as follows:

(1) *Detection of Na^+.*—Heat to 100° and maintain at that temperature for 2–3 minutes in the presence of an excess of $ZnCO_3$. Centrifuge. Then examine for Na^+.

(2) *Detection of K^+.*—Add an excess of NaOH and drive off any NH_3 by boiling. Make the solution acid with acetic acid to detect K^+. The ions Cs^+ and Rb^+ interfere.

If however it is desired to examine for the alkaline earths as well, it is simpler to use the solution prepared for the detection of these (see p. 151).

Visible spectrum.—Yellow line 587–589 mμ too sensitive for use.
Coloration of the flame is yellow, too sensitive.

CAESIUM

$Cs_2(PtCl_6)$ is less soluble than the potassium salt and its colour is yellower. The phosphomolybdate is less soluble than those of K^+ or NH_4^+.

Coloration of the flame is violet-rose.

Spectrum: blue doublet 455–459 mμ.

RUBIDIUM

Intermediate between K^+ and Cs^+.

Flame colour pink-violet. Violet doublet at 420–428 mμ.

These two elements are detected spectroscopically.

LITHIUM

Li = 6·94

Lithium, although technically a member of the first group of the periodic table, resembles in many of its properties typical alkaline earths. The hydroxide is much weaker than the other alkali hydroxides: $pK_A = 13·7$. The nitrate is soluble in alcohol and ether, as is calcium nitrate. The chloride dissolves in boiling pyridine which permits the separation of lithium from the other alkali metals. The list of slightly ionized compounds shows analogies with the alkaline earths.

Slightly soluble compounds

$Li_2C_2O_4$ . . . . . . 0·08M	Li_3PO_4 . . . . . . 0·001M
Li_2CO_3 . . . . . . 0·17M	Ferriperiodate . . . 0·0002M
LiF . . . . 0·10M	

Li_3PO_4 and Li_2CO_3, which correspond to acids of which the last dissociation constants are very small, are soluble not only in acids, but also in solutions of ammonium salts. LiF and LiC_2O_4 are soluble in strong acid.

Detection.—*Ferriperiodate reagent.*—The ferriperiodate complex gives a white precipitate of lithium ferriperiodate, $LiKFeIO_6$, in alkaline solution at 45–50°.

Solution required.—Dissolve 1 g of KIO_4 in 10 ml of 2N-KOH. Then dilute to 50 ml and add 3 ml of 0·5M-$FeCl_3$. Dilute to 100 ml with 2N-KOH.

Procedure.—Add 2 drops of reagent to 1 drop of solution. Heat to 50°. Make a blank test.

Concentration limit.—5 . 10^{-3} g.-ion of Li^+ per litre or 40 p.p.m.

Interfering substances.—NH_4^+, the alkaline earths, and the elements of the other groups all interfere. Hence Li^+ must be sought after suitable prior separations, as follows. 1 drop of the solution containing the alkaline earths is brought to the boil with 2 drops of 4N-NaOH and 1 drop of 30 per cent Na_2SO_4. NH_3 must be driven off completely before adding the sulphate. Centrifuge off the sulphates and the $Mg(OH)_2$, then carry out the test with the ferriperiodate complex.

Visible spectrum.—Red line at 671 mμ.

Flame coloration.—Deep red, specific in the absence of Sr.

ALKALINE EARTH GROUP

GENERAL CHARACTERISTICS

COLUMN IIa of the periodic classification contains the following elements:

Ia	IIa	IIIa
Li	Be $\uparrow$	B
Na	Mg $\longrightarrow$ Al	
K	Ca	
Rb	Sr	
Cs	Ba	
Fa	Ra	

The acidity of the cations increases from the bottom to the top, Be^{2+} is an acid; it has a tendency to give $Be(OH)_2$ which precipitates at pH 5 and above. In alkaline solution anions containing beryllium are formed. Mg^{2+} is less acid, $Mg(OH)_2$ precipitates at pH 10·6 and gives no anions. Ca^{2+}, Sr^{2+} and Ba^{2+} are no longer acid; they correspond to fairly strong bases. $Ba(OH)_2$ is the strongest base of them all.

We know that the acidity increases from left to right. Thus Li^+, Na^+, K^+, Rb^+, Cs^+ correspond to strong bases, B^{3+} is so acid that, even in very acid solution, it is present as HBO_2. Al^{3+} is more acid than Mg^{2+}, its hydroxide precipitates at pH 4, and it gives the AlO_2^- anions in alkaline solution. Summarizing, Al^{3+} and Be^{2+} are similar and, in analysis, we find them together. For the same reasons Li^+ is similar to Ca^{2+}.

Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} are in the same analytical group; Mg^{2+} differs a little from the other three. The differences are a little greater towards the top of the classification. The metals are all very strong reductants, though their reducing power diminishes in passing from barium to beryllium.

CALCIUM—STRONTIUM—BARIUM

$$Ca = 40·1; \quad Sr = 87·6; \quad Ba = 137·4$$

Only one state of oxidation in solution, II$^+$.

Redox.—The normal potential is of the order of $-3·0$ volts to $-2·7$ volts. The metals are strongly reducing and react with H^+ ions. The ions cannot be reduced except by electrolysis.

Hydroxides.—Strong bases in the second dissociation stage, and fairly strong in the first:

$$Ba(OH)_2 + H^+ \longrightarrow BaOH^+ + H_2O$$

$$Ba^{2+} + H_2O \rightleftharpoons BaOH^+ + H^+$$
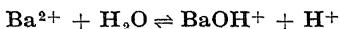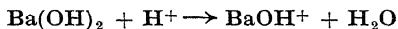
pK$_1$ = 13·3 for barium, 13·2 for strontium, and 12·6 for calcium.

The solubility of the hydroxides is rather small: $Ca(OH)_2$ is almost completely precipitated by 2N-NaOH.

Colourless cations; no anions.

Complexes.—Some of the complexes are rather unstable. Hydroxylated organic compounds (sugars, citrate ions, etc.) have a slight tendency

to form complexes, but this tendency is too slight to interfere with certain precipitations. The trilons (or complexons) give complexes which are a little more stable. Thus trilon B or ethylenediamine tetra-acetate, H_4R

$$\begin{array}{ccc} \text{HOOC.CH}_2 & & \text{CH}_2\text{.COOH} \\ & \diagdown\text{N—CH}_2\text{:CH}_2\text{—N}\diagup & \\ \text{HOOC.CH}_2 & & \text{CH}_2\text{.COOH} \end{array}$$
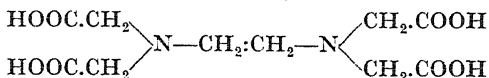
gives $HCaR^-$ and CaR^{2-}.

The polyphosphates and in particular the hexametaphosphate ion inhibit the precipitation of certain low-solubility compounds.

Ca^{2+} gives sulphate complexes.

Summarizing, the properties in solution are not outstanding. No redox reactions, no very stable complexes. However (difference from the alkali metals), a great number of low-solubility compounds.
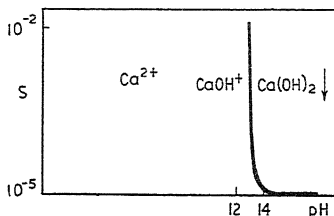
FIG. 34.—APPARENT SOLUBILITY OF CALCIUM HYDROXIDE AS A FUNCTION OF *p*H
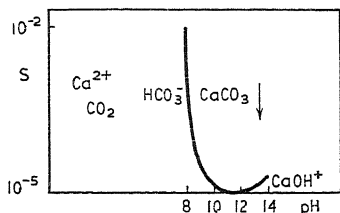
FIG. 35.—APPARENT SOLUBILITY OF CALCIUM CARBONATE AS A FUNCTION OF *p*H

Low-solubility compounds.—Carbonates.—As for a large number of low-solubility alkaline earth salts, the rate of precipitation is small in the cold, greater in the hot, whence the need to heat in order to precipitate the carbonates. Soluble in ammonium salt solutions, $CaCO_3$ and $BaCO_3$ can be used for buffering solutions at around *p*H 6 (see fig. 35).

Oxalates.—The calcium salt is the least soluble. They dissolve in acids, because oxalic acid is a weak acid in its second dissociation, $pk_1 = 4 \cdot 1$. The solubility of $Ca(C_2O_4)$ at *p*H 3 is low (acetic acid); but the difference of solubility is too small to permit a separation of Ca^{2+} from Ba^{2+}. $Ca(C_2O_4)$, of very low solubility, precipitates in very fine particles which can pass through filters.

Chromates.—Chromic acid is a weak acid in its second dissociation. $pk_1 = 6 \cdot 4$. Chromates are soluble in acids, apart from the less-soluble $BaCrO_4$ which is still rather insoluble in acetate-buffered solution. In this way a partial separation of Sr^{2+} and a complete separation of Ca^{2+} can be effected.

Sulphates.—$CaSO_4$ is much more soluble than the other two: its saturated solution slowly precipitates $SrSO_4$ and $BaSO_4$.

H_2SO_4 has an acidity constant $pk_1 = 1 \cdot 9$. $BaSO_4$ dissolves slightly in the concentrated acid when hot; $SrSO_4$, with a larger solubility product, dissolves more in acid solution, and $CaSO_4$ much more.

$CaSO_4$ crystallizes with $2H_2O$ and its crystals may be observed under the microscope. Sulphate complexes are formed with Ca^{2+}, which are less stable in the hot.

Phosphates.—The neutral phosphates, such as $Ca_3(PO_4)_2$, are of very low solubility in alkaline solution, but the third dissociation constant of phosphoric acid is negligible and, below pH 7, $CaHPO_4$ precipitates.

Ferrocyanides.—In neutral solutions of ammonium salts or in acetic acid $Ca(NH_4)_2(Fe(CN)_6)$ is of low solubility. Ba^{2+} can precipitate in concentrated solution. Mg^{2+} gives the same reaction.

Equilibrium constants

	Ca^{2+}	Sr^{2+}	Ba^{2+}
$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+$	12·6	13·2	13·3
$M(OH)_2 \downarrow \rightleftharpoons M^{2+} + 2OH^-$	3·4–5·1	3·5	1·8
$MCrO_4 \downarrow \rightleftharpoons M^{2+} + CrO_4^{2-}$	−0·2	4·4	9·7
$MSeO_4 \downarrow \rightleftharpoons M^{2+} + SeO_4^{2-}$	0·6	5·0	7·0
$M(IO_3)_2 \downarrow \rightleftharpoons M^{2+} + 2IO_3^-$	5·7	9·6	8·9
$MSO_3 \downarrow \rightleftharpoons M^{2+} + SO_3^{2-}$	4·0	7·4	8·0
$MSO_4 \downarrow \rightleftharpoons M^{2+} + SO_4^{2-}$	4·2	6·6	10·0
$MHPO_4 \downarrow \rightleftharpoons M^{2+} + HPO_4^{2-}$	5·3–6·6	—	—
$MCO_3 \downarrow \rightleftharpoons M^{2+} + CO_3^{2-}$	8·3	8·8–10·0	8·3
$MHCO_3^+ \rightleftharpoons M^{2+} + HCO_3^-$	− 0·8	—	—
$MC_2O_4 \downarrow \rightleftharpoons M^{2+} + C_2O_4^{2-}$	8·6	7·2	6·8
$M_3(PO_4)_2 \downarrow \rightleftharpoons 3M^{2+} + 2PO_4^{3-}$	25	—	—
$MF_2 \downarrow \rightleftharpoons M^{2+} + 2F^-$	10·4	8·5	5·8
$BaMnO_4 \downarrow \rightleftharpoons Ba^{2+} + MnO_4^{2-}$			9·6
$Ba(BrO_3)_2 \downarrow \rightleftharpoons Ba^{2+} + 2BrO_3^-$			5·3
$BaSeO_3 \downarrow \rightleftharpoons Ba^{2+} + SeO_3^{2-}$			7·0
$BaS_2O_3 \downarrow \rightleftharpoons Ba^{2+} + S_2O_3^{2-}$			4·0
$BaCit^- \rightleftharpoons Ba^{2+} + Cit^{3-}$			2·3

$Ca(NH_3)_6^{2+} \rightleftharpoons Ca(NH_3)_5^{2+} + NH_3$; $pk_6 = 1 \cdot 7$; $pk_5 = - 1 \cdot 3$; $pk_4 = - 1 \cdot 1$; $pk_3 = - 0 \cdot 8$; $pk_2 = - 0 \cdot 6$; $pk_1 = - 0 \cdot 2$ for $I = 2$.

Detection.—The elements other than the alkalis and alkaline earths must be separated before the alkaline earths are characterized (see p. 150).

Detection of Ba^{2+} and Sr^{2+}.—*Sodium rhodizonate.*—Sodium rhodizonate gives with Ba^{2+} and Sr^{2+} red compounds of low solubility. According to the concentration, a precipitate or a coloration is obtained. The Ba^{2+} compounds are less soluble than those of Sr^{2+} so that the reaction is less sensitive with the latter.
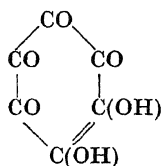
Rhodizonic acid

In 0·25N-HCl, strontium rhodizonate at the usual concentrations is completely redissolved and its colour disappears, whilst that due to Ba^{2+} is still visible under these conditions. On the other hand, when chromate is present, barium rhodizonate is not formed, whilst that of strontium remains (see the solubility of the chromates in the table).

By a combination of these reactions Sr^{2+} and Ba^{2+} can be detected. Unfortunately the reagent is rather unstable.

Solutions required.—(1) Solid sodium rhodizonate (or 'THQ'). The reagent must be kept in a tightly stoppered flask. It can be oxidized by the air, more rapidly in the light or in solution. When the reagent has not been used for some time, it is as well to check before use that it still gives the reaction.

Prepare a little rhodizonate solution (or 'THQ' solution) by addition of a few grains to 2–3 ml of water. The solution should be a fairly deep yellow. It does not keep.

(2) $0 \cdot 5N$-$HCl(1/25)$.

(3) 10 per cent K_2CrO_4.

Procedure.—The reactions are best carried out on paper. A drop of the neutral solution and a drop of the reagent are deposited on a piece of filter paper some distance from one another. The two solutions come into contact with one another by diffusion and a red coloration indicates the presence of one at least of the two ions. Add 2 drops of $0 \cdot 5N$-HCl, the coloration due to the strontium disappears slowly. Complete decoloration thus indicates the presence of Sr^{2+} alone. In the other case, Ba^{2+} alone or a mixture of Ba^{2+} and Sr^{2+} may be present.

Repeat the test as follows: to a drop of solution, add a drop of chromate; wait for a minute, then add a drop of reagent. A red coloration appears in the presence of Sr^{2+}.

Note.—In the presence of small quantities of barium (10^{-2} to 10^{-4} g.-ion/litre) a red coloration is still observed, which however disappears more or less rapidly when $N/2$ acid is added. The deduction of the presence of Sr may therefore be false: after the chromate has been precipitated, no coloration is produced. For this reason it is best in all cases to make the test with chromate.

Concentration limit.—$5 \cdot 10^{-4}$ g.-ion of Ba^{2+} or of Sr^{2+} per litre (30 and 70 p.p.m.). After separation with chromate: 10^{-3} g.-ion of Sr^{2+} per litre, or 90 p.p.m.

(1) **Detection of Ca^{2+}.**—As oxalate.—If the solution contains both Ba^{2+} and Sr^{2+}, separate them as sulphates, then precipitate the Ca^{2+} as the oxalate.

Solutions required.—Ammonium sulphate solution, saturated.
Ammonium oxalate solution, saturated (4·5 per cent).

Procedure.—Take 2 drops of the solution. Boil. Add 2 drops of ammonium sulphate. Leave for 10 minutes on the water bath. Centrifuge. Add 2 drops of ammonium oxalate to the supernatant liquid. Warm. Wait.

Concentration limit.—$5 \cdot 10^{-4}$ g.-ion of Ca^{2+} per litre, or 20 p.p.m.

(2) **As $CaSO_4.2H_2O$.**—Calcium sulphate is formed and the crystals are examined under the microscope (bundles of needles or sometimes of prisms with oblique ends).

Procedure.—Evaporate 1 drop of the solution under test to dryness on a micro slide. Take up the residue in 1 drop of H_2O and 1 drop of $2N$-H_2SO_4.

11

Concentration limit.—5.10^{-4} g.-on of Ca^{2+} per litre, or 20 p.p.m.

Interfering substances.—The reaction can only be carried out on solutions which contain no other elements besides the alkaline earths and the alkalis.

1 part of Ca^{2+} can be detected in the presence of 50 parts of Ba^{2+} or Sr^{2+}.

Coloration of the flame

Strontium: bright red, specific in the absence of Li.

Barium: pale green; many substances give blue or green colorations (see p. 341).

Calcium: orange-red, not specific.

Visible spectrum

Calcium: double yellow-orange band 602–618 mμ. Green band 552–554 mμ: when the salt is dissolved in HCl, other bands are obtained: 443 mμ, 593 mμ.

Strontium: Orange-yellow, 604 mμ, 606 mμ; blue, 461 mμ.

Barium: Intense green bands; weaker yellow-orange and blue ones; 614 mμ red; 553 mμ green; 487 mμ green. The chloride gives lines at 514 and 524 mμ in addition.

MAGNESIUM

Mg = 24·32

Magnesium is similar to beryllium and zinc. It has only one state of oxidation in solution : II^{+}.

Redox.—$E_0(Mg^{2+}/Mg) = -2\cdot4$ volts (calculated). The metal is a powerful reductant. It reduces H^{+} slowly in water, and rapidly in acids. It precipitates the majority of the elements As, Sb, Sn, Cd, etc., from their ions.
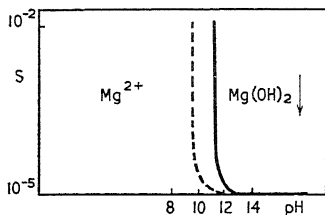
FIG. 36.—APPARENT SOLUBILITY OF $Mg(OH)_2$ AS A FUNCTION OF pH

Hydroxide.—$Mg(OH)_2$. This is a fairly strong base: $pk_1 = 11\cdot9$. The colourless cations are weakly acid. The 0·01M solution precipitates at about pH 10·6, and the precipitation is complete at around pH 12. See the adjoining curve of solubility of the hydroxide as a function of pH. However, the particles grow in course of time and the solubility diminishes. The aged precipitate redissolves at pH 9·5 (0·01M) and at pH 11·0 (10^{-5}M). The s.p. varies from $10^{-8\cdot8}$ to $10^{-10\cdot9}$.

Caustic soda and NH_3 precipitate $Mg(OH)_2$. The hydroxide is fairly soluble at a pH as low as 9·2 obtained with a buffer mixture of ammonia and an ammonium salt. The salts of weak acids, such as carbonates, borates, silicates, etc., added gradually to a solution of a magnesium salt, precipitate $Mg(OH)_2$ as soon as a suitable pH is attained. The corresponding salts can be precipitated, if they are insoluble, when a large

excess of reagent is added; in general a mixture of hydroxide and the salt is obtained.

$MgNH_4PO_4$ and Mg oxinate, which are less soluble than the hydroxide, can be precipitated in slightly less alkaline solution. In order to avoid the precipitation of $Mg(OH)_2$ the initial Mg salt solution should be acid, and should then be buffered with an ammonium salt–ammonia mixture. In this way the solubility of the salts is diminished simply by adding a large excess of ammonia. Several divalent ions give similar precipitates.

Magnesium hydroxide (or oxide) buffers acid solutions (and Mg^{2+} buffers alkaline solutions) at pH 9–10.

Complexes.—Very unstable ammoniates are formed up to $Mg(NH_3)_6{}^{2+}$; also $MgHCO_3{}^+$, $MgNO_3{}^+$, etc.

More stable complexes are the tartrates, metaphosphates, and those with the trilons, etc.

Equilibrium constants

$$Mg^{2+} + H_2O \rightleftharpoons MgOH^+ + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 11 \cdot 7$$

$$Mg(OH)_2 \downarrow \rightleftharpoons Mg^{2+} + 2OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 8 \cdot 8 - 10 \cdot 9$$

$$MgC_2O_4 \downarrow \rightleftharpoons Mg^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad . \quad 4 \cdot 1$$

$$Mg_3(PO_4)_2 \downarrow \rightleftharpoons 3Mg^{2+} + 2PO_4{}^{3-} \quad . \quad . \quad . \quad . \quad . \quad 12 \cdot 6$$

$$MgCO_3 \downarrow \rightleftharpoons Mg^{2+} + CO_3{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad . \quad 5 \cdot 0$$

$$MgF_2 \downarrow \rightleftharpoons Mg^{2+} + 2F^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 8 \cdot 2$$

$$MgNH_4PO_4 \downarrow \rightleftharpoons Mg^{2+} + NH_4{}^+ + PO_4{}^{3-} \quad . \quad . \quad . \quad . \quad 12 \cdot 6$$

$$Mg(NH_3)_6{}^{2+} \rightleftharpoons Mg(NH_3)_5{}^{2+} + NH_3; \quad pk_6 = -1 \cdot 3, \quad pk_5 = -0 \cdot 9$$
$$pk_4 = -0 \cdot 7, \quad pk_3 = -0 \cdot 4, \quad pk_2 = -0 \cdot 15;$$
$$pk_1 = +0 \cdot 2 \text{ for } I = 2$$

$$Mg \text{ oxine}_2 \downarrow \rightleftharpoons Mg^{2+} + 2 \text{ oxine}^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 16 \cdot 6$$

Detection.—All elements other than the alkaline earths, the alkalis and $NH_4{}^+$ must be separated first before proceeding to the detection of Mg^{2+} (see p. 150).

(1) **Thiazole yellow J or 'Titan yellow'.**—Magnesium hydroxide has the property of adsorbing numerous dyes, in particular thiazole yellow, which is thereby transformed from yellow to red. A precipitate or a coloration is obtained, depending upon the concentrations.

Solutions required
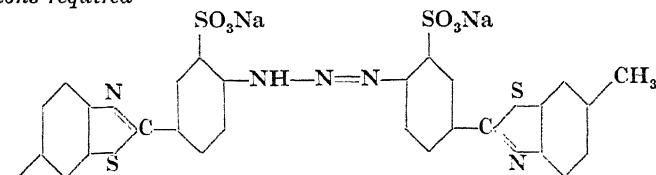
Thiazole yellow
(Colour index No. 813.)

Aqueous solution (0·1 per cent) of titan yellow.
0·1N caustic soda.

Procedure.—To 5 drops of 0·1N-NaOH add 1 drop of the reagent, then 1 drop of the solution completely neutralized.

Concentration limit.—3.10^{-4} of Mg^{2+} per litre, or 7 p.p.m.

Interfering substances.—Li^+ gives a salmon pink coloration. Much NH_4^+ interferes, and caustic soda must be added to bring the pH to a value sufficient to cause the precipitation of the hydroxide; Ca^{2+} in large quantities and very alkaline solution gives an orange precipitate or coloration by the formation of $Ca(OH)_2$. It is more correct therefore to detect Mg^{2+} after ammonium salts have been eliminated by ignition. Detection of Mg^{2+} should therefore be effected at the same time as that of the alkaline earths (see p. 150).

Ag^+, Hg^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} give the same reaction. Numerous hydroxides which precipitate interfere.

(2) **Hydroxyquinoline or oxine.**—In ammoniacal solution, a precipitate of magnesium oxinate $Mg(C_9H_6NO)_2$ is formed; this has a very low solubility. Note the difference from the alkalis and alkaline earths.
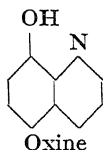
Oxine

Solutions required.—Saturated solution of oxine in ammonia–ammonium chloride buffer (0·2 per cent, approximately, dissolves).

Procedure.—Add 1 drop of solution to 2 drops of the reagent.

Concentration limit.—10^{-4} g.-ion of Mg^{2+} per litre, or 2 p.p.m. In U.V. there is a greenish-yellow fluorescence. The limit of sensitivity can then be 5.10^{-5}, or 1 p.p.m.

Interfering ions.—A large number of ions also precipitate oxine at pH 9. The precipitates with Be^{2+}, Al^{3+}, Pb^{2+}, Sb^{3+} are also fluorescent. Ca^{2+}, Ba^{2+}, Sr^{2+}, do not interfere.

DETECTION OF THE ALKALINE EARTHS AND OF THE ALKALIS DURING THE COURSE OF THE ANALYSIS

Preliminary test with ammonium sulphate.—The low solubility of the sulphates of barium and strontium can be utilized.

Procedure.—Introduce 1–2 drops of the solution into a drop of saturated ammonium sulphate: the formation of a white precipitate indicates the presence of Ba^{2+} or Sr^{2+} or both (or perhaps Ca^{2+} also, if it is present in large quantity, or of Pb^{2+}). If there is no precipitate, it is unnecessary to look for Ba^{2+} and Sr^{2+}.

Concentration limit.—Ba^{2+} 10^{-3}, Sr^{2+} 10^{-2}, Pb^{2+} 10^{-3}, Ca^{2+} > 1 g.-ion/litre.

Elimination of interfering substances.—The alkaline earths are detected after separation of the elements of the other groups. The solution thus contains only alkaline earths and the alkalis.

Principle.—The pH is adjusted to 9·0 by means of ammonia-ammonium chloride mixture: a certain number of hydroxides precipitate. The addition of ammonium sulphide causes sulphides of low solubility in alkaline solution to precipitate. The solution contains, besides the alkalis and the alkaline earths, elements whose sulphides redissolve

in an excess of sulphide. The solution is acidified, and these sulphides are reprecipitated. A solution is thus obtained containing no other elements besides the alkalis, the alkaline earths, and NH_4^+. The latter will have been detected before this in the initial solution.

When the solution contains arsenates or phosphates, Ca^{2+}, Ba^{2+}, Sr^{2+}, and Mg^{2+} will be precipitated during the separation (pH 9). The phosphate ions must therefore be eliminated in advance in acid solution. Only after this are the separations indicated made.

Treatment of the solution for the detection of the alkaline earths and the alkalis.—(*a*) **Phosphate absent**

Solutions required.—Freshly prepared ammonium sulphide. It should not give a precipitate with Ba^{2+} (indicating absence of CO_3^{2-} and SO_4^{2-}).

    12N- and 0·5N-HCl.

    Saturated ammonium chloride.

    15N-ammonia.

    Universal indicator paper.

Procedure.—In a 5–6 ml test-tube heat 30 drops of the solution on a water bath. Add 4 drops of ammonium chloride. Take off the water bath. Add 12 drops of ammonia, and then 5 drops of ammonium sulphide. Numerous sulphides and hydroxides precipitate. As, Sn, Sb, Mo, W, traces of Cu, and the alkaline earths and alkalis remain in solution. Stir with a thin stirrer. Centrifuge.

Detach the precipitate which adheres to the walls of the tube with a stirrer wetted with the clear solution. Centrifuge. Decant the supernatant liquor. Add 12N-HCl 5 drops at a time until the solution has a pH about 0. (Check by removing a drop on a stirring rod on to a piece of universal indicator paper.) Centrifuge. Evaporate the clear solution to dryness, ignite gently in order to drive off the ammonium salts. Take up with a drop of 0·5N-HCl. Add 30 drops of water. Warm. The solution is now ready for the detection of alkaline earths and the alkalis.

Notes.—(1) Black nickel sulphide can remain suspended in the colloidal state, during the first centrifuging. It is flocculated by the acidification and it develops sufficiently fast to remain insoluble in N-HCl.

(2) The solution containing the alkalis and the alkaline earths can contain colloidal sulphur. It can be freed from this by boiling with a few bits of (ashless) filter paper.

(*b*) Phosphates present

Solutions required.—Pure acetic acid.

    20 per cent solution of lead acetate.

Procedure.—30 drops of solution are heated on the water bath in a 5–6 ml test-tube. A drop of methyl red is added, then ammonia until it just turns colour. 15 drops of acetic acid are added, then 5 drops of lead acetate. All the phosphate is thus precipitated as lead phosphate. Leave for a minute on the water bath. Centrifuge. Check that precipitation is complete by adding 2 drops of lead acetate. Decant the supernatant solution. Add 6 drops of ammonium chloride solution, then 30 drops of ammonia. Then proceed as before.

Detection of Ba^{2+}, Sr^{2+}, Ca^{2+}.—Classical method

Principle.—Buffer the solution by adding a little ammonium acetate and precipitate the barium as chromate; Sr^{2+} and Ba^{2+} remain in solution. Add ammonium sulphate in concentration sufficient to precipitate the strontium and to maintain the calcium sulphate in solution as a complex.

Precipitate the calcium as the oxalate.

Solutions required

Ammonium acetate	30 per cent
Potassium chromate	10 ,, .,
Ammonium sulphate	saturated
Ammonium oxalate	5 per cent

(1) Detection of barium

Procedure.—To 2 drops of solution, add 2 drops of ammonium acetate. Boil. Add 1 drop of chromate. Barium gives a yellow precipitate.

Concentration limit.—$5 . 10^{-4}$ g.-ion of Ba^{2+} per litre, or 70 p.p.m.

Interfering substances.—Sr^{2+} precipitates slowly if its concentration is above 1M.

(2) **Detection of strontium.**—The preceding solution is centrifuged. The supernatant liquor should be yellow, indicating that excess chromate is present. Remove 2 drops of the clear solution and boil. Add 2 drops of ammonium sulphate. Leave for 6 minutes on the water bath.

Strontium gives a white precipitate.

Concentration limit.—10^{-9} g.-ion of Sr^{2+} per litre, or 100 p.p.m.

(3) **Dectection of calcium.**—The preceding solution is centrifuged. Calcium is detected on 2 drops of the clear solution.

Detection of Ba^{2+}, Ca^{2+}, Sr^{2+}, rapid method.—We have seen (p. 146) how Ba^{2+} and Sr^{2+} can be characterized by means of rhodizonate. Ca^{2+} is detected after the separation of the sulphates (p. 150).

AMMONIA GROUP

BERYLLIUM. ALUMINIUM. IRON. CHROMIUM. RARE EARTHS. TITANIUM. ZIRCONIUM. THORIUM. NIOBIUM. TANTALUM. URANIUM. GALLIUM. INDIUM. THALLIUM

THE ions of this group can exist in the following states of oxidation: Be(II), Al(III), Sc(III), Y(III), Tl(III), rare earths (III), and Ce(IV), Ti(IV), Zr(IV), Hf(IV), Th(IV), Nb(V), Ta(V) and also Fe(III), Cr(III), Si(IV), U(IV), Mn(III), Mn(IV), Co(III), Bi(III), V(IV), etc.

The hydroxides precipitate in $NH_3 + NH_4^+$ solution. They are frequently colloidal and have marked adsorptive properties.

Numerous complexes are formed with hydroxylated organic ions, with oxalates, fluorides, etc.

Few low-solubility compounds, apart from the phosphates. The sulphides are soluble.

Sn(IV), Sn(II), Ge(IV), and Ge(II) are similar to this group, although their sulphides are of low solubility. The same applies to Ga(III), In(III), and U(VI).

Place of the ammonia group elements in the periodic table

Ia	IIa	IIIa	IVa	Va	VIa	VIIa
Li(I)	Be(II)	B(III)	C(IV)			
Na(I)	Mg(II)	Al(III)	Si(IV)			
	Ca(II)	Sc(III)	Ti(IV)	V(V)	Cr(VI)	Mn(VII)
	Sr(II)	Y(III)	Zr(IV)	Nb(V)	Mo(VI)	Tc(VII)
	Ba(II)	R.E.(III)	Hf(IV)	Ta(V)	W(VI)	Re(VII)
	Ra(II)	Ac(III)	Th(IV)	Pa(V)	U(VI)	
					etc.	

The cations increase in acidity in the direction of the arrows.

The ammonia group includes the elements whose cations are sufficiently acid for the hydroxides to be formed in ammonia–ammonium chloride solution, i.e. at pH 9·2, and insufficiently acid for them to be in the anionic state at the same pH. These elements are thus those in the centre of the classification.

In Column IIa, there is only one element which belongs to the group: this is Be(II), similar not to B, which is too acid, but to Al(III).

In column IIIa, B(III) forms a soluble hydroxide $B(OH)_3$; we shall find it among the anions. Al^{3+}, Sc^{3+}, Y^{3+} and the rare earths belong to the ammonia group. They are decreasingly acid from Al to the rare earths, the latter being of quite low acidity.

In column IVa, all the members are very acid. CCl_4 is insoluble in

water, and is not hydrolysed. H_2CO_3 exists, as do the anions HCO_3^- and CO_3^{2-}. $SiCl_4$ is hydrolysed giving H_2SiO_3, and the corresponding anions are slightly more basic than the corresponding carbonate anions. Ti^{4+}, Zr^{4+}, Hf^{4+}, Th^{4+}, very acid, are part of the ammonia group. Ti and Zr do exist in solution in the form of cations which are still very acid.

In column Va, Nb and Ta are part of the group. The hydroxides do not dissolve except in concentrated acid and in very concentrated alkali, yielding cations and anions of very little importance. They remain, in general, among the insolubles along with silica.

In column VIa, only the last element is a part of the group, in the form of the slightly acid cation UO_2^{2+}. The other elements are too acid and scarcely exist in any other form than the anionic one in solution, so that they are not precipitated by ammonia.

Iron (III) and chromium (III) belong to the ammonia group. Fe^{3+} and Cr^{3+} are acids.

Tl^{3+}, In^{3+}, Ga^{3+}, column IIIb, may be considered as similar to the ammonia group in the properties of their hydroxides.

Precipitation pH's of the hydroxides.—The hydroxides precipitate in the following order from solutions of their chlorides, when the acidity of the solution is decreased:

Si(IV), Ta(V), Nb(V), Sn(IV), Zr(IV), Ti(IV), Th(IV), Ga(III), In(III), Al(III), Sc(III), rare earths (III), Be(II).

General reagents.—(1) *Adsorption compounds.*—A large number of dyes (in particular the 'chromatable' dyes) are adsorbed by, or give adsorption compounds with, the hydroxides, or maybe compounds with basic ions. As a result a colour change occurs.

The principal reagents which have been proposed are hydroxylated derivatives of anthraquinone, hydroxyazo dyes, cochineal, morin, aluminon, haematoxylin, etc.

The stability of these compounds as a function of pH follows the same order as that of the precipitation pH's of the hydroxides. Thus, among the ions more frequently met with, only Zr(IV) often reacts in very acid solution and the reaction is then specific. Only Be(II) frequently reacts in strong alkali. Similarly Th(IV) reacts in sufficiently acid solution to be detected in the presence of the rare earths.

Between these two extremes, it is not possible to render the reactions specific by pH adjustment, if small quantities of an element are being sought in the presence of a large quantity of a neighbouring element.

It is hardly possible to utilize the formation of complexes, because the stabilities of those that are known are too near to one another to permit easy differentiation.

(2) *Fluorescence* is sometimes much more selective than colour reactions. Thus chrome blue does not give a fluorescence except with Ga(III) and Al(III).

(3) *Precipitating reagents.*—Certain reagents also precipitate the different ions in more or less the same order as they are precipitated as hydroxides. In strong acid solution, arsenic and phosphoric acids only precipitate a small number of ions: those of Zr(IV), Ti(IV), Th(IV), Sn(IV), Ce(IV), Nb(V), Ta(V).

Phosphoric acid in 2–3N-HCl has been proposed for characterizing Zr.

Arsenic acid permits a selective separation of Zr and Ti which can be utilized for the external characterization of titanium.

The arsonic acids give more complete and more sensitive precipitations.

The characterization is more sensitive when azoarsonic compounds are used, as these yield coloured precipitates. Thus, with *p*-dimethylaminoazophenylarsonic acid, Zr(IV) can be characterized with certainty and sensitivity in the presence of other cations.

Separations.—*Cupferron* in 1·5N-HCl effects a quantitative separation of all the elements before Ga from those following it in the list above (p. 154).

The precipitate and the excess of reagent can be rapidly removed with ethyl acetate. Al^{3+} can then be detected.

Oxine can also be used, in particular, in order to separate Ga^{3+} and Al^{3+}. Here also the precipitate can be removed by extraction with chloroform.

ALUMINIUM

$$Al = 26·97$$

State of oxidation.—Aluminium has analogies with beryllium, on the one hand, and with iron and chromium, when their oxidation number is III, on the other. In solution it is always in the same state of oxidation III^+.

Influence of *p*H.—Al^{3+} is colourless. The hydroxide, $Al(OH)_3$, which is white, precipitates above *p*H 3·8 (0·01M) and redissolves in solutions of *p*H 10–12·6, depending on its degree of development, giving the colourless anion AlO_2^-.
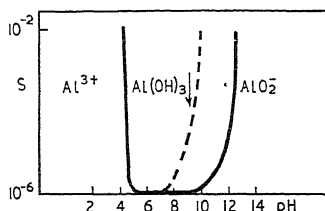
FIG. 37.—APPARENT SOLUBILITY OF ALUMINIUM HYDROXIDE AS A FUNCTION OF *p*H

$Al(OH)_3$ easily becomes colloidal, but it ages rapidly in alkaline solution in the hot. The low-solubility hydroxide precipitates from low-alkalinity aluminate solutions.

Complexes.—These are numerous. The principal ones are those derived from the anions of hydroxylated organic compounds: citrates, tartrates, etc.

The fluoride complexes, AlF^{2+}, $Al(AlF_6)$, $Na_3(AlF_6)$, the last two having a rather low solubility, and the oxalates, $Al(C_2O_4)_2^-$ and $Al(C_2O_4)_3^{3-}$, are fairly stable.

Low-solubility compounds.—There are not many of these: the phosphate $AlPO_4$ and the oxinate are the most important. This latter is

soluble in chloroform. Caesium alum $Al_2(SO_4)_3$, Cs_2SO_4, $24H_2O$ is of fairly low solubility.

The rather unstable acetate complex is destroyed on heating, with precipitation of the hydroxide.

Equilibrium constants

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad 4{\cdot}9$$
$$AlOH^{2+} + 2H_2O \rightleftharpoons Al(OH)_3 \downarrow + 2H^+ \quad . \quad . \quad . \quad . \quad . \quad 3{\cdot}9$$
$$Al(OH)_3 \downarrow \rightleftharpoons Al^{3+} + 3OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 32{\cdot}7$$
$$Al(OH)_3 \downarrow \rightleftharpoons H_2AlO_3^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad 12{\cdot}6{-}15$$
$$Al(C_2O_4)_2^- \rightleftharpoons Al^{3+} + 2C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad . \quad 13{\cdot}0$$
$$Al(C_2O_4)_3^{3-} \rightleftharpoons Al(C_2O_4)_2^- + C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad 3{\cdot}3$$
$$AlF_6^{3-} \rightleftharpoons AlF_5^{2-} + F^-; \quad pk_6 = 0{\cdot}5; \quad pk_5 = 1{\cdot}6; \quad pk_4 = 2{\cdot}7;$$
$$pk_3 = 3{\cdot}9; \quad pk_2 = 5{\cdot}0; \quad pk_1 = 6{\cdot}1{-}6{\cdot}3$$
$$Na_3(AlF_6) \downarrow \rightleftharpoons 3Na^+ + AlF_6^{3-} \quad . \quad . \quad . \quad . \quad . \quad . \quad 27$$
$$Al(AlF_6) \downarrow \rightleftharpoons Al^{3+} + AlF_6^{3-} \quad . \quad . \quad . \quad . \quad . \quad . \quad 9{\cdot}4$$
$$Al\ oxine_3 \downarrow \rightleftharpoons Al^{3+} + 3\ oxine^-. \quad . \quad . \quad . \quad . \quad . \quad 32{\cdot}3$$
$$Al\ cupferron_3 \downarrow \rightleftharpoons Al^{3+} + 3\ cupferron^- \quad . \quad . \quad . \quad . \quad . \quad 18{\cdot}6$$

Redox.—The normal potential of the Al/Al^{3+} system is $-1{\cdot}5$ to $-1{\cdot}7$ volts. The metal is a powerful reductant, but it covers itself with a protective film of the oxide. When the oxide film is removed, attack proceeds fast; this can be achieved either by making aluminium amalgam, the Al_2O_3 floats off, or else by dissolving Al at a pH of less than 5 or greater than 11.

Al precipitates Ag, Cu, Hg, Sn, Sb, Cd, etc., from their ions by reduction.

Detection

Aluminon.—Ammonium aurine tricarboxylic acid (aluminon) turns from pink to red in acetate buffered solution, probably due to the
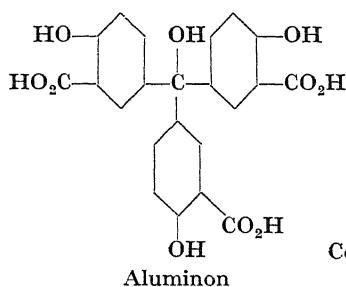
Aluminon   Colour Index, 727;
                            Schultz, 557.

formation of an internal complex as a result of the juxtaposition of —COOH and the —OH groups in the ortho position to one another.

Solutions required.—Aluminon in aqueous solution, 0·1 per cent.

Acetate buffer: sodium acetate 56 g, 24 ml of glacial acetic acid: make up to 100 ml.

Note.—The acetate solution gradually attacks the glass and a little aluminium goes into solution.

Procedure.—On a test plate, to 1 drop of the solution to be examined, add

1 drop of reagent and 2 drops of the buffer solution. Wait for a few minutes.

When the concentration of aluminium is low, compare the solution with a blank containing the reagent and the buffer solution.

Concentration limit.—10^{-4} g.-ion/litre, or 3 p.p.m.

Interfering substances.—(1) The colour of the aluminon changes in alkaline solution; hydroxides precipitate. In too acid solution, the aluminium is present as Al^{3+} and the reaction does not occur. Hence the need to use an acetate buffer.

(2) Powerful oxidants at pH 4·5 destroy the dye: Au(III), Ce(IV), Cr(VI).

(3) Certain other ions give colorations; these are: intense colorations—Be(II), Fe(III), Ti(IV), Ga(III), and Sc(III); slight colorations—Bi(III), B(III), Cr(III), Hg(II), Mo(VI), V(IV), Zr(IV), and Th(IV).

Certain ions interfere by superimposition of their own colours; these are: Cu(II), Co(II), and V(V).

Elimination of interfering substances.—(1) **With cupferron.**—Fe(III), Mo(VI), V(V), Ti(IV), and Ga(III) can be separated from aluminium by cupferron in 1·5N-HCl. The compounds formed and the excess of the reagent can be separated by extraction with ethyl acetate. V(IV) should be oxidized beforehand to V(V) and Fe(II) to Fe(III).

Solution required.—6 per cent aqueous solution of cupferron, freshly prepared.

Procedure.—Add 1 drop of 4N-HCl and 2 drops of cupferron to 1 drop of the solution to be examined in a microcone. Then add 10–15 drops of ethyl acetate. Shake. Draw off the aqueous solution below the ethyl acetate with a dry pipette. Make the test on 1 drop of the solution. The separation is very rapid and is quantitative.

Cu^{2+}, Ni^{2+}, Co^{2+} must be complexed by the addition of 20 per cent cyanide. On an indicator spot plate, add 1 drop of 20 per cent cyanide to 1 drop of the solution under test. Stir with a drawn-out stirring rod. The precipitate should redissolve in the excess of cyanide. When this occurs, proceed as before.

Precious metals should be separated after reduction if they are present.

(2) **With caustic soda.**—The elements whose hydroxides are of low solubility can be separated by rendering the solution alkaline.

Procedure.—To 1 drop of solution, add 4 drops of 2N-NaOH. Boil. Centrifuge. Then take 1 drop of the clear solution. Compare it with a blank made up from 1 drop of the same 2N-NaOH, 1 drop of the reagent, and 2 drops of buffer solution.

Remarks about eliminations.—(1) If the separation is effected with cupferron, only Be^{2+} which accompanies the Al^{3+} can give the same reaction.

(2) If the separation is made with caustic soda, the majority of the Be^{2+} remains with the Al^{3+} and so does the Ga^{3+}.

Hence, if Be^{2+} is present, Al^{3+} must be sought with 'chrome blue', after separating with cupferron when Ga^{3+} is present.

Notes.—(1) The absence of a reaction to aluminon in acetate buffer indicates the absence of the following elements: Be(II) $10^{-3.5}$, Fe(III) 10^{-4}, Ti(IV) 10^{-2}, Ga(III) 10^{-4}, Sc(III) 10^{-4}, Cr(III) 10^{-1}, V(IV) 10^{-2}, Zr(IV) 10^{-3}, Th(IV) 10^{-4} g.-ion/litre.

(2) The absence of a precipitate with cupferron in $1.5N$-HCl indicates the absence of a number of important ions: Sn(IV) 10^{-4}, Zr(IV) 10^{-4}, Fe(III) $10^{-3.7}$, V(V) $10^{-3.5}$, Mo(VI) $10^{-3.5}$, Ga(III) $10^{-3.3}$, Ti(IV) $10^{-3.3}$, Bi(III) $10^{-3.3}$, W(VI) $10^{-2.3}$ g.-ion/litre.

Morin.—Morin or pentahydroxy-3,5,7,2′,4′-flavone gives, with the majority of the ions of the aluminium group, a fluorescence varying from greenish blue to yellow. With Al^{3+} a good sensitivity is obtained at pH 4·5.
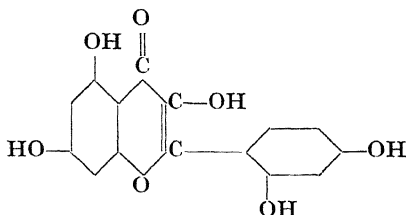
Solutions required.—0·005 per cent solution of morin in alcohol.
Buffer solution (see aluminon).

Procedure.—Add 1 drop of the reagent to 4 drops of solution, and then add 4 drops of buffer solution. If there is a precipitate, separate it, then add a further drop of the reagent before examining the fluorescence.

Concentration limit.—4.10^{-4} or 10 p.p.m. In U.V., 10^{-4} g.-ion/litre, or 3 p.p.m.

Interfering substances.—More or less the same as in the case of aluminon. Eliminate them in the same way. Only Be^{2+} can then interfere, if its concentration is high (10^{-1} g.-ion/litre).

'**Chrome blue**'.—Among the hydroxyazo dyes, those which have the group
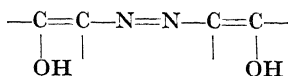
give a very selective fluorescence with Al^{3+} and Ga^{3+}.

In particular 2,2′ hydroxy-4-sulpho-naphthalene-azo-naphthalene gives an orange-coloured fluorescence: acid chrome blue 2R Bayer, chrome blue black NR, blue black Pontachrome R or Solochrome blue black BS.
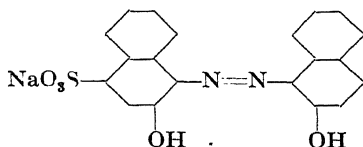
Colour Index, 202; Schultz, 181.

Solution required.—0·01 per cent aqueous solution of the dye. Acetate buffer (see p. 156).

Procedure.—Add 1 drop of the dye solution, 1 drop of the buffer, and 3 drops of alcohol to the solution to be investigated. Warm.

Observe in a dark room in the light from a Wood's lamp. When Al^{3+} is present, an orange coloration will be observed. A blank generally shows negligible fluorescence. The tests can be made in glass tubes.

Concentration limit.—This depends on the intensity of the U.V. light used; it is about 10^{-6} g.-ion/litre, or 0·03 p.p.m. The reaction is thus very sensitive.

Interfering substances.—Very few ions give marked fluorescences. Only Ga^{3+} gives a red fluorescence. Same sensitivity as with Al^{3+}.

Coloured ions diminish the intensity of the fluorescence and, as a result, they diminish the sensitivity of the reaction: Cr(III) and U(VI) slightly; Co(II) and Mo(VI) considerably; Ni(II), Cu(II), Fe(III), Ti(IV), V(IV), and V(V) quench the fluorescence.

Fe(II) interferes because, at pH 4·5, it is oxidized fairly rapidly in the air to Fe(III).

Ions which precipitate Al^{3+} diminish or quench the fluorescence according to their concentration: this applies to much phosphate and arsenate.

Ions which are sufficiently oxidizing destroy the reagent: Tl(III), Au(III), Pt(IV).

Cr(VI) does not interfere much. It slightly diminishes the sensitivity of the reaction on account of its colour.

Ions which form complexes with Al^{3+}: $C_2O_4^{2-}$, F^-, diminish or quench the fluorescence; they must be eliminated before any analysis for cations.

Elimination of interfering substances.—(1) Fe(III), Mo(VI), Ti(IV), and Ga(III), can be separated from aluminium by cupferron in 1·5N-HCl. The compounds formed and the excess of the reagent are separated by extraction with ethyl acetate. V(IV) should be first oxidized to V(V) and Fe(II) to Fe(III), see aluminon (p. 157).

(2) Co^{2+}, Cu^{2+} can be complexed by the addition of 20 per cent cyanide, sufficient just to cause the first-formed precipitate to be redissolved. Then only Co^{2+} diminishes the sensitivity on account of the yellow colour of the cobalticyanide.

(3) The oxidants, Ce(IV), Tl(III), if present, should be reduced, for example by the addition of a small quantity of bisulphite. The excess of SO_2 is then driven off by boiling. Precious metals should be separated by reduction, then filtration. It should be noted that Be^{2+} does not interfere (distinction from what happens with most of the other reagents for Al^{3+}).

BERYLLIUM

Be = 9·02

Beryllium is similar in some respects to aluminium, and in some to magnesium. It exists in only one state of oxidation II+.

Redox.—The element is a powerful reductant. $E_0 = -1·7$ volt (calc.).

IIa	IIIa
Be(II)	B(III)
↑ Mg(II)→Al(III)	

Influence of pH.—The cations Be^{2+} are first formed, then $BeOH^+$ which condenses into Be_2OH^{3+} and Be_2O^{2+}, which are colourless. White $Be(OH)_2$ precipitates at a pH of around 6·0 (0·01M). It redissolves at about pH 13·5, giving the anions BeO_2^{2-} and $Be_2O_3^{2-}$ which are colourless. The hydroxide is thus not very soluble in $NH_3 + NH_4^+$ solution, a fact which differentiates it and permits its separation from Mg^{2+}. The alkaline solution precipitates at the boil, giving the hydroxide which is much less soluble.
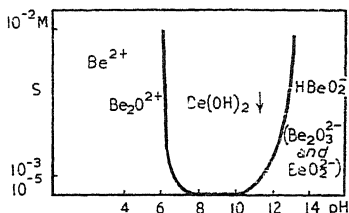
FIG. 38.—APPARENT SOLUBILITY OF BERYLLIUM HYDROXIDE AS A FUNCTION OF pH

Low-solubility compounds.—NH_4BePO_4 is less soluble than the hydroxide: it has only a low solubility in acetate buffer (difference from Mg^{2+}). Beryllium oxinate, like that of magnesium, is soluble at pH 4·5 and not much soluble in ammoniacal solution (separation from Al^{3+}).

Complexes.—Citrates and tartrates, fairly stable. $Be(OH)_2$, freshly prepared, dissolves in solutions of the alkali carbonates, whence boiling reprecipitates it (difference from Al^{3+}).

Equilibrium constants

$$2Be^{2+} + H_2O \rightleftharpoons Be_2O^{2+} + 2H^+ \quad \ldots \ldots \quad 6·4; \ 6·9$$
$$Be(OH)_2 \downarrow \rightleftharpoons Be^{2+} + 2OH^- \quad \ldots \ldots \quad 20·0$$
$$Be(OH)_2 \downarrow \rightleftharpoons BeO_2^{2-} + 2H^+ \quad \ldots \ldots \quad 29·7$$
$$H_2Be_2O_3 \downarrow \rightleftharpoons Be_2O^{2+} + 2OH^- \quad \ldots \ldots \quad 18·4$$
$$H_2BeO_3 \downarrow \rightleftharpoons Be_2O_3^{2-} + 2H^+ \quad \ldots \ldots \quad 29·1$$
$$BeF_2 \downarrow \rightleftharpoons Be^{2+} + 2F^- \quad \ldots \ldots \quad \sim 2$$
$$BeF_4^{2-} \rightleftharpoons BeF_3^- + F^-; \quad pk_4 = 2·0; \quad pk_3 = 3·6; \quad pk_2 = 5·0;$$
$$pk_1 = 4·3–5·9$$
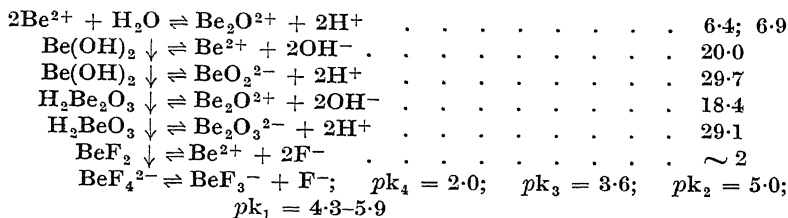
Detection.—**Morin.**—Morin gives a yellow fluorescence with Be^{2+} in alkaline solution.

Solutions required.—0·02 per cent morin in alcohol. 4N-NaOH.

Procedure.—2 drops of solution, 1 drop of reagent, and 3 drops of 4N-NaOH are placed in succession in a microcone.

The yellow fluorescence, which can be seen even in daylight, should be examined in U.V. light.

Concentration limit.—This depends on the intensity of the U.V. light. We

have found that the fluorescence is still strong at 10^{-4} g.-ion/litre, or 1 p.p.m.

Interfering substances.—(1) Very few substances give a marked fluorescence. Li^+ in large quantities gives a slight one. Sc(III) which redissolves slightly in alkaline solution, and so may be present, gives a slight one also. Much Zn(II) gives a slight fluorescence, which can be caused to disappear by addition of cyanide. Much Ca(II) gives a slight fluorescence which can be made to disappear by addition of pyrophosphate.

(2) Numerous hydroxides precipitate in alkaline solution, and the precipitates adsorb morin and frequently give a fluorescence. The hydroxides should therefore be separated after their complete precipitation, and before adding the reagent.

Coloured ions diminish or inhibit the fluorescence. There are not many that can do this under the conditions of test: Cr(III) in concentration of 0·1 g.-ion/litre displaces the concentration limit to 10^{-5} g.-ion/litre. The precious metals, Au(III), Pt(IV), should be separated. U(VI), W(VI), V(IV), V(V) diminish the sensitivity.

IRON

$Fe = 55·8$

States of oxidation.—II^+ in the ferrous ions which put iron into the zinc group; III^+ in the ferric ions which are found in the ammonia group; and VI^+ in the ferrates which are analogous to the manganates and chromates.

Fe(II)

When its oxidation number is II iron is similar to Mn(II), Zn(II), Ni(II), Co(II) whose common properties are described on page 187.
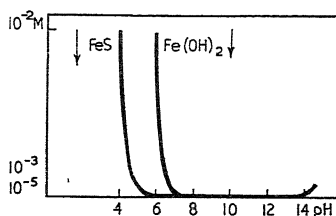
FIG. 39.—APPARENT SOLUBILITIES OF FERROUS HYDROXIDE
AND SULPHIDE AS A FUNCTION OF pH

Influence of pH.—Fe^{2+},aq., pale green, is acid, less so than Fe^{3+},aq.

$Fe(OH)_2$ (white) starts to precipitate at pH 5·8. It oxidizes rapidly in the air to green, then black, ferro-ferric hydroxides, then becomes rust-coloured from the formation of ferric hydroxide. $Fe(OH)_2$ scarcely dissolves in very strong alkali.

Complexes.—Like Ni^{2+}, Zn^{2+}, etc., Fe^{2+} gives ammonia complexes. They oxidize rapidly in the air. Complexes formed with hydroxylated organic compounds, with hypophosphites and oxalate ions. Very stable

complexes with *o*-phenanthroline (see p. 167) and with cyanide ions: $Fe(CN)_6{}^{4-}$.

Low-solubility compounds.—A large number of ferrous compounds have a low solubility: the carbonate, cyanide, oxalate, phosphate, etc. The black sulphide FeS precipitates above pH 4, and it oxidizes slowly in air; in the colloidal state, the solution is a deep green.

Equilibrium constants

$$Fe(OH)_2\downarrow\ \rightleftharpoons Fe^{2+} + 2OH^-. \quad . \quad . \quad . \quad . \quad 18{\cdot}5$$
$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+ \quad . \quad . \quad . \quad . \quad 5{\cdot}9$$
$$Fe(OH)_2\downarrow\ \rightleftharpoons HFeO_2{}^- + H^+ \quad . \quad . \quad . \quad . \quad 18{\cdot}5$$
$$FeS\downarrow\ \rightleftharpoons Fe^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad 18{\cdot}4{-}21{\cdot}6$$
$$FeCl^+ \rightleftharpoons Fe^{2+} + Cl^- \quad . \quad . \quad . \quad . \quad 0{\cdot}3$$
$$Fe(C_2O_4)\downarrow\ \rightleftharpoons Fe^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad 6{\cdot}7$$
$$Fe(C_2O_4)_3{}^{4-} \rightleftharpoons Fe^{2+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad 6{\cdot}2{-}10{\cdot}0$$
$$FeCO_3\downarrow\ \rightleftharpoons Fe^{2+} + CO_3{}^{2-} \quad . \quad . \quad . \quad 10{\cdot}3$$
$$FeCrO_4\downarrow\ \rightleftharpoons Fe^{2+} + CrO_4{}^{2-} \quad . \quad . \quad . \quad 5{\cdot}6$$
$$Fetart._2{}^{2-} \rightleftharpoons Fe^{2+} + 2tart.^{2-} \quad . \quad . \quad . \quad 4{\cdot}9$$
$$Fe(2,2'\text{-dipyridyl})_3{}^{2+} \rightleftharpoons Fe^{2+} + 3(\text{dipyridyl}) \quad . \quad . \quad 15{\cdot}0$$
$$Fe(1,10\text{-}o\text{-phenanthroline})_3{}^{2+} \rightleftharpoons Fe^{2+} + 3\text{-}o\text{-phenanthroline} \quad . \quad 17{\cdot}7$$

Fe(III)

When its oxidation number is III, Fe finds its place in the Al^{3+} group.

Influence of pH.—In acid solution, Fe^{3+} is always present. It is colourless or slightly mauve (perchloric or nitric acid solutions). In sulphuric or hydrochloric acid solution, yellow complexes are formed.

The rust-coloured hydroxide precipitates from a pH of 2·2 upwards (0·01M) but it can remain colloidally disperse right up to the neutral point. It is very slightly amphoteric; at first it goes into colloidal solution in small quantities, then it dissolves properly in very strong alkali as $FeO_2{}^-$.

In the presence of Fe(II), the green or black ferro-ferric hydroxide can come down.

FIG. 40.—APPARENT SOLUBILITY OF FERRIC HYDROXIDE AS A FUNCTION OF pH

Complexes.—The number of complexes formed is very large: lemon-yellow chlorides, intense red thiocyanates such as $FeCNS^{2+}$ all unstable, unstable red acetates such as $Fe(CH_3COO)_2{}^+$, which are destroyed at elevated temperatures with precipitation of the hydroxide; colourless fluorides among which FeF^{2+}, $FeF_6{}^{3-}$ give salts, of which even those with the alkali metals are of low solubility; pyrophosphates, phosphates and complexes with hydroxylated organic compounds; green oxalates which are more stable. Very stable complexes: ferricyanides $Fe(CN)_6{}^{3-}$ and nitroprussides (ferrinitrocyanides) $Fe(CN)_5NO^{2-}$ both orange-yellow.

Low-solubility compounds.—Few of the compounds are less soluble than the hydroxide: $FePO_4$ is of low solubility in acetic acid

solution. Basic ions such as CO_3^{2-}, BO_2^- in general give a precipitate of the hydroxide when a suitable pH is attained.

Ammonium sulphide precipitates black Fe_2S_3 stable only in alkaline solution; H_2S precipitates $FeS + S$.

Organic solvents.—Cupferron and oxine give compounds which can be extracted with chloroform or carbon tetrachloride. $Fe(CNS)_3$ (or $Fe[Fe(CNS)_6]$) gives a red solution in many organic solvents. The chloride can be extracted with ether from solutions containing much HCl; the compound involved is yellow $HFeCl_4$.

Equilibrium constants

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad \ldots \qquad 2\cdot2$$
$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \qquad \ldots \qquad 4\cdot7$$
$$Fe(OH)_3 \downarrow \rightleftharpoons Fe^{3+} + 3OH^- \qquad \ldots \qquad 37\cdot4\text{--}38\cdot2$$
$$Fe_2S_3 \downarrow \rightleftharpoons 2Fe^{3+} + 3S^{2-} \qquad \ldots \qquad 88$$
$$FeCl^{2+} \rightleftharpoons Fe^{3+} + Cl^- \qquad \ldots \qquad 1\cdot4$$
$$Fe(CNS)_5^{2-} \rightleftharpoons Fe(CNS)_4^- + CNS^-, \text{ etc.}; \quad pk_5 = 0\cdot02;$$
$$pk_4 = 0\cdot8; \quad pk_3 = 1\cdot4; \quad pk_2 = 1\cdot9;$$
$$pk_1 = 2\cdot1(I = 1); = 2\cdot9 \ (I = 0)$$
$$FeHPO_4^+ \rightleftharpoons Fe^{3+} + HPO_4^{2-} \qquad \ldots \qquad 9\cdot4$$
$$FeHCit^+ \rightleftharpoons Fe^{3+} + HCit^{2-} \qquad \ldots \qquad 6\cdot3$$
$$FeTart^+ \rightleftharpoons Fe^{3+} + Tart.^{2-} \qquad \ldots \qquad 33\cdot3$$
$$FeF_5^{2-} \rightleftharpoons FeF_4^- + F^-; \quad pk_5 = 0\cdot5; \quad pk_4 = 2\cdot2$$
$$pk_3 = 3\cdot0; \quad pk_2 = 4\cdot2; \quad pk_1 = 5\cdot5 \ (I = 0\cdot5)$$
$$FeS_2O_3^+ \rightleftharpoons Fe^{3+} + S_2O_3^{2-} \qquad \ldots \qquad 2\cdot7$$
$$FeN_3^{2+} \rightleftharpoons Fe^{3+} + N_3^{2-} \qquad \ldots \qquad 4\cdot3$$
$$Fe(C_2O_4)_3^{3-} \rightleftharpoons Fe(C_2O_4)_2^- + C_2O_4^{2-}; \quad pk_3 = 4\cdot0; \quad pk_2 = 6\cdot8;$$
$$pk_1 = 9\cdot4 \ (I = 0)$$
$$Fe(oxine)_3 \downarrow \rightleftharpoons Fe^{3+} + 3 \text{ oxine}^- \qquad \ldots \qquad 31\cdot8, 47$$
$$Fe(oxine)^{2+} \rightleftharpoons Fe^{3+} + \text{oxine}^- \qquad \ldots \qquad 14\cdot5 \ (I = 0)$$
$$Fe(cupferron)_3 \downarrow \rightleftharpoons Fe^{3+} + 3(cupferron)^- \qquad \ldots \qquad 25\cdot0$$

Redox.—(1) $Fe \downarrow - 2e \rightleftharpoons Fe^{2+}$; $E_0 = -0\cdot44$ volt. The reaction is slow in both directions. Iron is a strong reductant and is easily oxidized, in particular by dilute acids: $Fe \downarrow + 2H^+ = Fe^{2+} + H_2 \uparrow$

It is attacked by oxygen in the presence of water. It can precipitate some metals (Sb, Ag, Pb, etc.) from aqueous solutions of their salts.

In alkaline solution, the formal potential is $-0\cdot8$ to $-0\cdot9$ volt in 10N-NaOH saturated with hydroxide. This is near to the potential at which hydrogen itself is discharged. Iron is attacked fairly rapidly when hot, very slowly in the cold: in both cases hydrogen is liberated. The main product is black Fe_3O_4 $(Fe(FeO_2)_2)$.

(2) $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E_0 = 0\cdot78$ volt.

(*a*) **In acid solution.**—In perchloric acid, the formal potential is $0\cdot7$ volt, independent of pH. In $0\cdot01$M solution, $Fe(OH)_3$ precipitates at pH $2\cdot2$, and as soon as this commences the potential drops rapidly while the pH increases (fig. 41).

In N-HCl the normal formal potential is $0\cdot65$ to $0\cdot69$, and in N-H_2SO_4 it is $0\cdot67$. In N-HNO_3, $0\cdot70$, in 2N-$HClO_4$, $0\cdot75$ and, in 5N-H_3PO_4 at pH 0 it is $0\cdot52$ volt.

12

In acid solution, the position of the Fe^{3+}/Fe^{2+} system on the scale of redox potential is the reason for the large number of oxidations by ferric salts and reductions by ferrous salts.
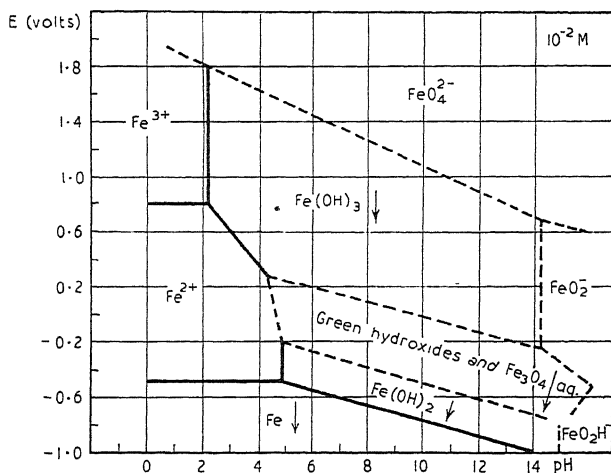
FIG. 41.—FORMAL POTENTIALS OF THE REDOX SYSTEMS OF IRON

Oxidizing properties of the ferric ions:

Action on H_2S:
$$2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + S \downarrow + 2H^+$$
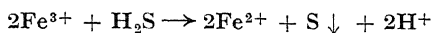
Action on iodides:
$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$
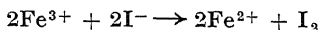
Action on stannous salts:
$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

Action on H_2SO_3:
$$2Fe^{3+} + H_2SO_3 + H_2O \longrightarrow 2Fe^{2+} + SO_4{}^{2-} + 4H^+$$
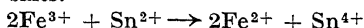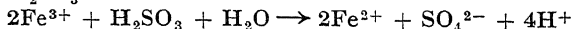
Action on thiosulphates:
$$2Fe^{3+} + 2S_2O_3{}^{2-} \longrightarrow 2Fe^{2+} + S_4O_6{}^{2-}$$
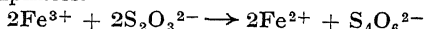
Reducing properties of ferrous ions:

Slow action of the air:
$$4Fe^{2+} + O_2 \uparrow + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$$

Action of permanganate:
$$MnO_4{}^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
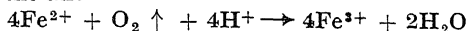
Action of nitrates:
$$NO_3{}^- + 2Fe^{2+} + 2H^+ \longrightarrow NO_2{}^- + 2Fe^{3+} + H_2O$$
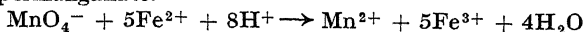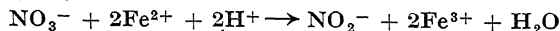
followed by:
$$HNO_2 + Fe^{2+} + H^+ \longrightarrow NO \uparrow + Fe^{3+} + H_2O$$
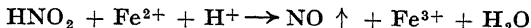
(b) **In alkaline solution**
$$Fe(OH)_2 \downarrow + OH^- - e \rightleftharpoons Fe(OH)_3 \downarrow$$
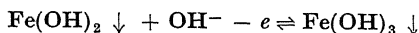
The formal potential is about -0.7 volt at pH 14 (fig. 41).

In neutral or alkaline solution, the oxidizing properties of ferric salts disappear. I_2 oxidizes Fe^{2+}, and NO_3^- can be reduced to NH_4^+ by $Fe(OH)_2$; the salts of silver, mercury, arsenic, bismuth, antimony, are reduced to the metallic state. Ferrous hydroxide absorbs oxygen rapidly. It oxidizes first to green, then to black (ferro-ferric hydroxides), then to the rust-red ferric hydroxide $Fe(OH)_3$.

In 10N-NaOH FeO_2^{2-} oxidizes rapidly in the air, slowly in water with precipitation of $Fe(FeO_2)_2$, black. Oxidants such as ClO^- then give $Fe(OH)_3$.

(3) $FeO_4^{2-} + 8H^+ + 3e \rightleftharpoons Fe^{3+} + 4H_2O$; $E_0 > 1.9$ volts at $pH\ 0$ and 0·6 to 0·70 volt in very strongly alkaline solution (calculated potentials). The ferrates are strongly oxidizing, and so are unstable. We do not meet then in analysis.

(4) Potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ (see p. 315).

Detection of Fe^{3+}

Thiocyanate.—Ferric salts give a red coloration with thiocyanates in acid solution by the formation of unstable complexes such as $Fe(CNS)^{2+}$, $Fe(CNS)_3$, $Fe(CNS)_6^{3-}$. In the presence of numerous organic solvents the equilibria are displaced in favour of $Fe(CNS)_3$ which is soluble in ether giving a red solution, and in benzyl alcohol giving a violet-red solution.

Solution required.—Saturated solution of ammonium thiocyanate.
Procedure.—Add 1 drop of reagent to 1 drop of the solution being examined, using a test plate.
Concentration limit.—5.10^{-5} g.-ions of Fe^{3+} per litre, or 3 p.p.m.

If 1 drop of reagent is added to 10 drops of solution the colour is easier to observe: 10^{-5}–5.10^{-6} g.-ion of Fe^{3+} per litre. In more dilute solution, a pale pink colour comparable with that of the reagents themselves, particularly with that of 'pure' HCl, is obtained.

Interfering substances.—(1) CNS^- is not basic, so that the test can be made in strong acid. Above $pH\ 2$–3, $Fe(OH)_3$ precipitates and the complex is destroyed. Hence it is essential to operate in strong acid.

(2) Oxidants can destroy CNS^-. Hence an excess of reagent must be used. HNO_2 and conc. HNO_3 interfere, because the oxidation products of CNS^- are coloured.

(3) The thiocyanate complexes of ferric iron are not of high stability so that even ions such as SO_4^{2-} and Cl^-, if present in large quantity, diminish the sensitivity of the reaction. Ions which form complexes with CNS^- such as Hg^{2+} must be counteracted by the addition of an excess of reagent.

See below for the ions which give colorations. Those which give weak colorations only decrease the sensitivity if they are present in large quantity.

Ti(IV), giving an orange colour, interferes when present in large quantity. Cu(II) is brown; add several drops of HSO_3^-, but the red colour due to the Fe(III) then disappears slowly due to reduction. In general, the colour due to Fe is so strong that it can be detected in the presence of that due to copper. However, if it is desired to demonstrate the presence of iron in the presence of a large amount of copper it is

best to proceed as follows: immediately after the addition of the bisulphite, add a little benzyl alcohol and shake. The ferric complex is extracted into the benzyl alcohol and is thus withdrawn from the reducing action of the sulphurous acid.

VO^{2+} gives a complex having a blue colour which is not soluble in benzyl alcohol.

Ni^{2+} in large quantity gives a pale green coloration which is not soluble in the organic solvent.

Note.—In the presence of large quantities of interfering ions, it is better to search for iron with *o*-phenanthroline, page 167.

Remarks on reactions with CNS^-.—Numerous ions give coloured complexes in acid solution. The concentration limits are indicated. The absence of a coloration indicates that all these ions are absent: Fe(III) red 5.10^{-5}, Bi(III) golden yellow 2.10^{-4}, U(VI) yellow 10^{-3}, Co(II) blue 2.10^{-2}, V(IV) violet to blue 10^{-2}; Ti(IV) orange 2.10^{-2}, or 3.10^{-3} in alcohol, Cu(II) brown 2.10^{-4}, Mo(IV) orange-red 10^{-3}, Re(VII) orange-red 10^{-3} g.-ion/litre. Nearly all these complexes are soluble in the alcohols. Only the compounds with Fe(III), Ti(IV), Mo(VI), Co(II) and to a small extent Cu(II) are soluble in ether. The sensitivity of the reactions is increased by organic solvents. The precious metals also give colorations.

Detection of Fe^{2+}

Dimethylglyoxime.—In the presence of NH_3, dime thylglyoxime gives a red coloration with ferrous ions due to the formation of a complex $Fe(C_4H_7N_2O_2)_2 . 2NH_3$.

$$CH_3—C\!\!=\!\!NOH$$
$$|$$
$$CH_3—C\!\!=\!\!NOH$$
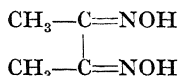
Solutions required.—(*a*) 1 per cent alcoholic solution of dimethylglyoxime or an aqueous solution of the sodium salt.

(*b*) Buffer solution:

NH_3 0·88	40 ml
NH_4Cl	20 g
Water	60 ml

The DMG can be made up as a 1 per cent solution in the buffer.

Procedure.—1 drop of solution under examination is placed in a microcentrifuge tube, 2 drops of the reagent added, followed by 2 drops of the buffer solution. Centrifuge if necessary, to see the coloration.

Concentration limit.—3 p.p.m. The limit is increased by atmospheric oxidation.

Interfering substances.—Fe(III) precipitates and can carry down Fe(II) as Fe_3O_4. Complex it before the buffer solution is added with an excess of solid sodium fluoride. However, in the presence of F^- and Cu(II), Fe(II) partially disappears by reducing Cu(II). Apart from this, much Cu(II) interferes by the blue colour of its ammino complexes. Mn(II) in high concentration oxidizes in the air, giving the colloidal brown oxide.

Co(II), in large quantities, interferes by its brown colour; moreover, it reduces Fe(III) in ammoniacal solution if not complexed.

Note.—Ni(II) gives a characteristic red precipitate. Addition of a crystal of persulphate causes the red colour due to Fe(II) to disappear and the Ni compound is then more easily observed.

o-phenanthroline and 2,2′-dipyridyl.—These two reagents give a very stable red complex with ferrous ions, containing three molecules of the reagent per Fe²⁺ ion.

o-phenanthroline and 2,2′-dipyridyl.—These two reagents give a very stable red complex with ferrous ions, containing three molecules of the reagent per Fe^{2+} ion.
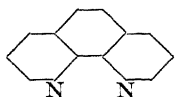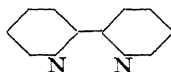
o-phenanthroline   2,2′-dipyridyl

Solutions required.—2 per cent aqueous solution of *o*-phenanthroline hydrochloride or a 2 per cent alcoholic solution of the base.

Procedure.—Add 1 drop of the reagent to a not too acid drop of the solution on a test plate.

Concentration limit.—10^{-5} g.-ion of Fe^{2+} per litre, or 0·5 p.p.m.

Interfering substances.—The reaction is practically specific.

The colours of coloured ions can interfere if the latter are present in strong concentration: by diluting the solution before test, this sort of interference is in general avoided. Fe^{3+} should be complexed by the addition of a small amount of solid fluoride.

Numerous ions take up the reagent on their own account (without giving a coloration). It is therefore necessary to add an excess.

To detect Fe^{2+} at a concentration of 3.10^{-5} g.-ion/litre, in the presence of:

0·5 g.-ion/litre of	Cu(II) or Zn(II)	.	add 10 drops of reagent.
,,	,,	Co(II), Sb(III), Bi(III)	,,	4	,,	,,
,,	,,	Cd(II)	,,	3	,,	,,
,,	,,	Hg(II), Ni(II)	,,	2	,,	,,

Only Co^{2+} and Cu^{2+} diminish the sensitivity; Co^{2+} forms an orange complex which reduces the sensitivity to 5.10^{-3} g.-ion of Fe^{2+} per litre, and Cu^{2+} forms a brown complex which reduces it to 10^{-3} g.-ion/litre. ClO_4^- precipitates red ferrous *o*-phenanthroline. Iridium gives a vermilion complex.

Detection of Fe^{3+}.—The reaction can be used after addition of a drop of bisulphite which reduces the ferric iron to the ferrous state.

Note.—If neither of these two reagents is available, Fe^{2+} should be detected with dimethylglyoxime (p. 166).

Fe(II) and Fe(III). Prussian blue.—The ferrocyanide ion gives with ferric ions a deep blue precipitate of ferric and potassium ferrocyanides of variable composition. This precipitate is sometimes colloidal, and slightly soluble in acids; it disappears in alkaline solution. The reaction can be formally depicted thus:

$$Fe(CN)_6^{4-} + Fe^{3+} \rightleftharpoons Fe^{III}[Fe^{II}(CN)_6]^-$$
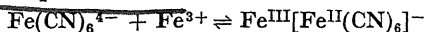
Similarly ferricyanide ions give a blue precipitate with ferrous ions having very similar properties:

$$Fe(CN)_6^{3-} + Fe^{2+} \rightleftharpoons Fe^{II}[Fe^{III}(CN)_6]^-$$

The redox equilibria:

$$Fe(CN)_6{}^{3-} + Fe^{2+} \rightleftharpoons Fe(CN)_6{}^{4-} + Fe^{3+}$$

and $$Fe^{III}(Fe^{II}(CN)_6)^- \rightleftharpoons Fe^{II}(Fe^{III})(CN)_6)^-$$
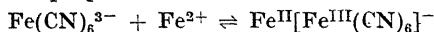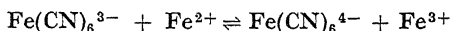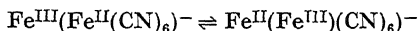
are set up, indicating that if we start at the same concentrations in either case, the final product will be the same, but the second equilibrium is established very slowly.

The colour of the blue precipitate is very intense and specific. It can therefore be utilized. But numerous ferrocyanides are of low solubility and coloured (see uranium, p. 183) and they considerably diminish the sensitivity of the reaction.

Ferrous ferrocyanide has a low solubility, and is white: it oxidizes in the air to the blue ferric ferrocyanide.

Ferric ferricyanide does not precipitate.

CHROMIUM

$$Cr = 52{\cdot}0$$

Oxidation numbers.—II in the chromous salts; III in the chromic salts, which are the more important ones, and are similar to those of Al(III) and Fe(III); VI in the chromates and dichromates.

Cr(II)

The chromous ions Cr^{2+} are blue. By increasing the pH, basic salts, white to blue in colour, are precipitated at around pH 6. The hydroxide develops rapidly, turning orange, brown, then black.

$$Cr(OH)_2 \downarrow \rightleftharpoons Cr^{2+} + 2OH^- \quad \ldots \quad 17$$

Ammine complexes are blue, not very stable in air. Cyanide complex stable around pH 5; the complex with CNS^- is blue and unstable.

An extremely powerful reductant, Cr^{2+}, is hardly ever encountered in qualitative analysis.
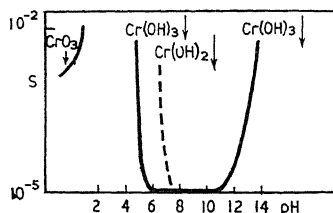
FIG. 42.—APPARENT SOLUBILITY OF THE HYDROXIDES OF Cr(VI), Cr(III) AND Cr(II) AS A FUNCTION OF pH

Cr(III)

Chromic ions, Cr^{3+} and $CrOH^{2+}$, are violet, whilst $Cr(OH)_3$ is grey. The latter precipitates from pH 4·6 (0·01M). It redissolves at pH 13–14 giving green $CrO_2{}^-$. By boiling the solution, $Cr(OH)_3$, in a less soluble form, is totally precipitated.

$Cr(OH)_3$ is often colloidal. It is flocculated when the hydroxides of iron and aluminium are precipitated, when these latter are present in large quantity. On the other hand, if $Cr(OH)_3$ predominates the flocculation of the other hydroxides is retarded.

Low-solubility compounds.—There are not many: greenish $CrPO_4$, soluble in acetic acid; the anhydrous chloride and sulphate only dissolve at an infinitely slow rate.

Complexes.—The chloride complexes are rather unstable. $CrCl_2^+$ and $CrCl^{2+}$ are green, $CrSO_4^+$, $Cr(SO_4)_2^-$, $Cr(SO_4)_3^{3-}$ are fairly stable; both acetates and the mauve ammines are destroyed on boiling their solutions; the oxalates, citrates, and cyanides are stable. Fluoride and thiocyanate complexes are also known.

Equilibrium constants

$$Cr^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H^+ \quad \ldots \quad \ldots \quad 3\cdot8; \; 4\cdot0; \; 3\cdot9$$
$$CrOH^{2+} + H_2O \rightleftharpoons Cr(OH)_2^+ + H^+ \quad \ldots \quad \ldots \quad 6\cdot2$$
$$Cr(OH)_3 \downarrow \rightleftharpoons Cr^{3+} + 3OH^- \quad \ldots \quad \ldots \quad 30\cdot3$$
$$Cr(OH)_3 \downarrow \rightleftharpoons H_2CrO_3^- + H^+ \quad \ldots \quad \ldots \quad 15\text{--}16$$
$$CrCl_2^+ + H_2O \rightleftharpoons CrOH^{2+} + H^+ + 2Cl^- \quad \ldots \quad 5\cdot7; \; 5\cdot4$$
$$CrCl_2^+ \rightleftharpoons Cr^{3+} + 2Cl^- \quad \ldots \quad \ldots \quad 1\cdot9(?)$$
$$Cr(CNS)_6^{3-} \rightleftharpoons Cr(CNS)_5^{2+} + CNS^-; \quad pk_6 = -1\cdot6; \quad pk_5 = -0\cdot7;$$
$$pk_4 = 0\cdot3; \quad pk_3 = 1\cdot0; \quad pk_2 = 1\cdot7;$$
$$pk_1 = 3\cdot1 \; (I = 0)$$
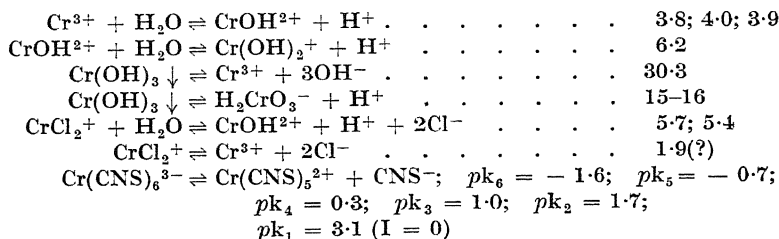
Cr(VI)

Its ability to exist in the state of oxidation VI puts chromium into the sixth group of the periodic table. It is similar in this state to V(V).

Va	VIa	VIIa
V(V)	Cr(VI) Mo(VI) W(VI) U(VI)	Mn(VII)

The acidity and the oxidizing power increase in the direction of the arrows.

The deep red CrO_3 is very soluble in water, less soluble in concentrated sulphuric and perchloric acids. There are no cations containing Cr(VI). CrO_2Cl_2 is a brownish red liquid, decomposed by water. Chromic acid is a strong acid in its first dissociation: $pk_2 = 0\cdot7$, $pk_1 = 6\cdot4$. It also exists in the form of condensed ions, mainly $Cr_2O_7^{2-}$ (orange) and to a very small extent as $Cr_3O_{10}^{2-}$ (red), $Cr_4O_{13}^{2-}$ (brown); CrO_4^{2-} is yellow.

Many chromates have a low solubility. The least soluble are $BaCrO_4$, Hg_2CrO_4 (brick red), $PbCrO_4$ (yellow); these are still of low solubility at pH 4; Ag_2SrO_4 (brick red) dissolves in NH_3 and HNO_3. The salts of Mg^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, and the alkalis, are soluble.

Coloured complexes CrO^{4+} and CrO^{2+} with hydrogen peroxide, soluble in ether.

Equilibrium constants

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \quad . \quad . \quad . \quad . \quad 0\cdot 7$$
$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \quad . \quad . \quad . \quad . \quad 6\cdot 4$$
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \quad . \quad . \quad . \quad . \quad . \quad 1\cdot 8; \, 1\cdot 7$$
$$CaCrO_4 \downarrow \rightleftharpoons Ca^{2+} + CrO_4^{2-} \quad . \quad . \quad . \quad -0\cdot 2$$
$$SrCrO_4 \downarrow \rightleftharpoons Sr^{2+} + CrO_4^{2-} \quad . \quad . \quad . \quad . \quad 4\cdot 4$$
$$FeCrO_4 \downarrow \rightleftharpoons Fe^{2+} + CrO_4^{2-} \quad . \quad . \quad . \quad . \quad 5\cdot 6$$
$$Ag_2Cr_2O_7 \downarrow \rightleftharpoons 2Ag^+ + Cr_2O_7^{2-} \quad . \quad . \quad . \quad 6\cdot 7$$
$$Hg_2CrO_4 \downarrow \rightleftharpoons Hg_2^{2+} + CrO_4^{2-} . \quad . \quad . \quad . \quad 8\cdot 7$$
$$BaCrO_4 \downarrow \rightleftharpoons Ba^{2+} + CrO_4^{2-} \quad . \quad . \quad . \quad . \quad 9\cdot 7$$
$$Ag_2CrO_4 \downarrow \rightleftharpoons 2Ag^+ + CrO_4^{2-} \quad . \quad . \quad . \quad 12\cdot 0; \, 11\cdot 4$$
$$PbCrO_4 \downarrow \rightleftharpoons Pb^{2+} + CrO_4^{2-} \quad . \quad . \quad . \quad . \quad 13\cdot 7$$

Redox.—(1) $Cr \downarrow -2e \rightleftharpoons Cr^{2+}$ $E_0 = -0\cdot 56$ volt.

In 8N alkali we have

$$Cr \downarrow +4OH^- -2e \rightleftharpoons CrO_2^{2-} + 2H_2O \quad E_0 = -1\cdot 00 \text{ volt}$$
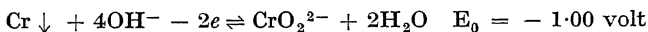
(solution saturated with the hydroxide).

The metal rapidly covers itself with a protective layer and becomes passive in nitric acid. HCl attacks it.

(2) $Cr^{2+} -e \rightleftharpoons Cr^{3+}$ $E_0 = -0\cdot 41$ volt.

Formal potentials.—$E'_0 = -0\cdot 40$ volt in 5N-HCl; $E'_0 = -0\cdot 37$ volt in $0\cdot 2$–$1N$-H_2SO_4.

In acid solution, the chromous salts are strong reductants. They oxidize rapidly in the air. They react slowly with hydrogen ions:

$$2Cr^{2+} + 2H^+ \rightleftharpoons 2Cr^{3+} + H_2 \uparrow$$
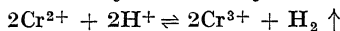
a reaction which can be accelerated by many catalysts, such as platinum. They reduce practically all other systems: ClO_4^-, NO_3^- to NH_4^+, Sn^{2+} (to Sn); Cr^{3+} is reduced to Cr^{2+} by zinc amalgam or zinc alone in acid solution.

In strong alkali, the hydroxide first oxidizes to a brownish black colour.

(3) $Cr(VI) + 3e \rightleftharpoons Cr(III)$.

In acid solution:

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \quad E_0 = 1\cdot 36 \text{ volts (calculated)}$$
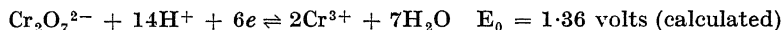
but the exchange of electrons is in general slow.

In very acid solution, $Cr_2O_7^{2-}$ oxidizes fairly fast.

Formal potentials.—$E'_0 = 1\cdot 19$ volts in N-$HClO_4$, $1\cdot 10$ volts in $0\cdot 2N$, $1\cdot 06$ volts in $0\cdot 1N$-$HClO_4$. For $Cr(VI)$ at $0\cdot 1N$, $E'_0 = 1\cdot 27$ volts in N-HNO_3; $E'_0 = 1\cdot 07$ volts in N-H_2SO_4, $1\cdot 10$ volts (2M), $1\cdot 30$ volts (6M), $1\cdot 34$ volts (8M); $E'_0 = 0\cdot 99$ to $1\cdot 09$ volts in N-HCl, $1\cdot 15$ volts (4N).

The reaction is slow at pH 2, and is catalysed by Fe^{2+}, $HAsO_2$, as well as by Sn^{2+} and $Fe(CN)_6^{4-}$. At pH 4·5 it is in general very slow; chromates are not reduced by the most powerful reductants. On the other hand, Cr^{3+} is oxidized only very slowly in acid solution, and then only by the very powerful oxidizing agents, MnO_4^- in excess and in the hot, for example; CrO_2^-, on the other hand, which exists in alkaline solution, is oxidized more rapidly.

$$CrO_2^- + 2H_2O -3e \rightarrow CrO_4^{2-} + 4H^+ \quad E_0 = -0\cdot 12 \text{ volt } (pH \, 14)$$
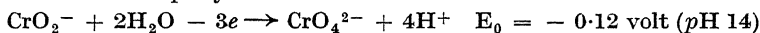
Intermediate oxides of low solubility are formed: $Cr(OH)CrO_4$ or $Cr_2(CrO_4)_3$.

At $pH < 1\cdot3$, iodine is oxidized by dichromates to iodate; at $pH > 1\cdot3$, iodate is reduced to iodine by chromium salts.
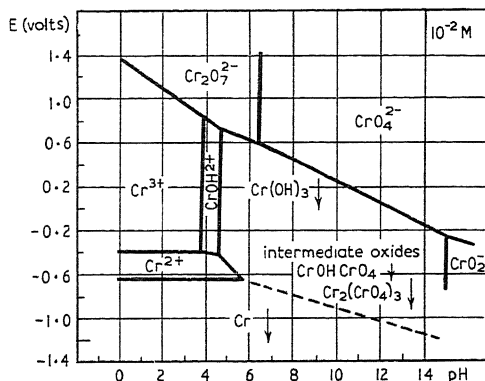
FIG. 43.—APPROXIMATE FORMAL REDOX POTENTIALS OF
THE REDOX SYSTEMS OF CHROMIUM

In alkaline solution, Cr(III) is easily oxidized by chlorine, bromine, hydrogen peroxide, lead dioxide, sodium peroxide, and the persulphates. Above pH 4·5 chlorine oxidizes Cr^{3+}.

Chromium sesquioxide is converted to a chromate by alkaline fusion.

$$Cr(CN)_6{}^{4-} - e \rightleftharpoons Cr(CN)_6{}^{3-} \quad E_0 = -1\cdot28 \text{ volts}$$
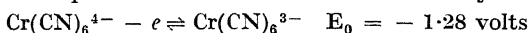
Detection

Cr(III) is oxidized to Cr(VI), which is then detected.

Oxidation in alkaline solution

Solutions required.—Caustic soda 4N.

Solid sodium or ammonium persulphate.

Procedure.—Add 3 drops of 4N-NaOH and a crystal of persulphate to a drop of the solution in a microcone. Boil, centrifuge.

A yellow coloration in the supernatant liquid is specific for the formation of chromate.

Concentration limit.—2.10^{-3} g.-ion of Cr^{3+} per litre, or 100 p.p.m.

Interfering substances.—If the caustic soda is too concentrated some Cu(II) or Cr(III) can pass into solution, giving colours which interfere. If this should occur, dilute, boil, and centrifuge again.

A bulky precipitate of the hydroxide can adsorb considerable quantities of chromate and thus diminish the sensitivity.

Ba^{2+} can precipitate as the chromate; Cr(III) can still be detected at a concentration of 10^{-2} in the presence of Ba^{2+} at 0·1 g.-ion/litre.

If Mn(II) and Ni(II) are present at the same time, the latter catalyses the oxidation of the former in alkaline solution and the violet colour of the permanganate appears. The solution should then be centrifuged, separated, acidified with $9N-H_2SO_4$ and the $MnO_4{}^-$ reduced with sodium nitrite (10 per cent) added drop by drop. The orange coloration of dichromate then appears.

Notes about oxidation by persulphates in alkaline solution.—The addition of caustic soda may throw down precipitates which it is useful to note. After boiling with persulphate, Mn(II), Ni(II), Co(II) are converted to peroxides which are brown to black. Ba(II) precipitates as the yellow chromate.

Detection of small quantities. Diphenylcarbazide

Reaction.—The inconvenience attending the above method of detecting Cr(III) as chromate can be avoided by redissolving the precipitate in acid and detecting the chromate with diphenylcarbazide, which the chromate oxidizes to give a violet coloration.

Solution required.—1 per cent alcoholic solution of diphenylcarbazide, freshly prepared (colourless or a very faint yellow).

Procedure.—The solution obtained as described above (i.e. after oxidation with persulphate, etc.) is boiled for 30 seconds to destroy the excess of persulphate. Acidify with 2 drops of $9N$-H_2SO_4. Cool. Add 1 drop of reagent. A violet coloration indicates the presence of chromium.

Concentration limit.—$4 \cdot 10^{-5}$ g.-ion of Cr^{3+} per litre, or 2 p.p.m.

Interfering substances.—Oxidants, including excess of dichromate, destroy the violet coloration.

Fe(III) and Mo(VI) interfere, giving colorations of their own. In this case add a little solid sodium fluoride to complex these before adding the reagent.

V(V) is the most troublesome. It gives an extremely sensitive red coloration. It should be separated with cupferron, which removes Fe(III) and Mo(IV) at the same time.

Procedure.—See Al^{3+}, page 157. (Keep a little of this solution for the later detection of Al(III) and Ga(III).)

Ni(II), Co(II), and Mn(II) are present as black peroxides which will not redissolve in acid solution. Centrifuge before adding the reagent.

Notes.—The absence of a black precipitate shows the absence of the following quantities of: Ni(II) $2 \cdot 10^{-3}$, Co(II) $2 \cdot 10^{-3}$, Mn(II) $5 \cdot 10^{-5}$ g.-ion/litre. The absence of a coloration with diphenylcarbazide shows the absence of V 10^{-4}, Fe(III) $2 \cdot 10^{-3}$, Mo(VI) $3 \cdot 10^{-2}$ g.-ion/litre as well as the absence of Cr.

RARE EARTHS

This is a series of very similar elements whose separation is very difficult. Their atomic numbers range from 57 to 71. Scandium and yttrium are generally taken with the rare earths which they follow in the separations. The cations of the rare earths are not very acid. The hydroxides precipitate at pH 6·8–8·5. Yttrium is very similar. Sc^{3+} is more acid and resembles Al^{3+} a little, whilst still remaining extremely similar to Y^{3+}.

IIIa
Al
Sc
Y
Rare earths
Ac

The precipitation pH's of the hydroxides in solution are: Sc, 6·1; Y, 7·0–7·8; Gd, 6·2; Lu, 6·0; Nd and Pr, 7·0–7·4; Yb, 6·2–7·1; Dy, 7·0; La, 7·3–8·4; Ce, 7·1–7·4; Sm, 6·8 (0·01M).

Ce^{3+}, Y^{3+}, Sc^{3+}, La^{3+} are colourless, Pr^{3+} is green, Nd^{3+} violet-pink, Er^{3+} pink, etc.

Basic salts such as $Sc(OH)_2Cl$ can precipitate in concentrated solution.

The oxalates have a low solubility in dilute acid. The fluorides are also of low solubility in acids. Some of the rare earths give low-solubility double sulphates with the alkali metals sulphates (the 'ceric earths').

Complexes.—Numerous. Formed with tartrate, citrate, and other ions.

Equilibrium constants

$$M(OH)_3 \downarrow \rightleftharpoons M^{3+} + 3OH^- \quad . \quad . \quad . \quad 19\text{--}23$$
$$M_2(C_2O_4)_3 \downarrow \rightleftharpoons 2M^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad 24\text{--}28$$
$$Y_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Y^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad 26\cdot3$$
$$Sc_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Sc^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad 14\cdot5$$
$$M_2(S_2O_3)_3 \downarrow \rightleftharpoons 2M^{3+} + 3S_2O_3{}^{2-} \quad . \quad . \quad 8\cdot6\text{--}11\cdot3$$
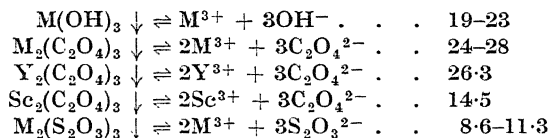
Redox.—The metals are strong reductants: $-1\cdot5$ to $-2\cdot2$ volts. In the II oxidation state the elements are almost as strongly reducing as in the metallic state; hence only a few elements are found in this state:

$$Eu^{3+} + e \rightleftharpoons Eu^{2+} \quad . \quad . \quad -0\cdot43 \text{ to } -0\cdot49 \text{ volt}$$
$$Yb^{3+} + e \rightleftharpoons Yb^{2+} \quad . \quad . \quad -0\cdot6 \text{ volt}$$
$$Sm^{3+} + e \rightleftharpoons Sm^{2+} \quad . \quad . \quad -0\cdot8 \text{ ,,}$$
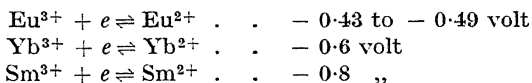
None of the elements exists in any higher state of oxidation than III with the exception of cerium: Ce^{4+}. The solid $PrO_2(Pr_6O_{11})$ is known: it is not very stable.

$$PrO_2 \downarrow + 4H^+ + e \rightleftharpoons Pr^{3+} + 2H_2O \quad E_0 > -1\cdot6 \text{ volts}$$
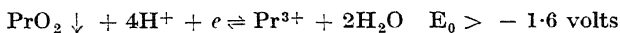
Separation of the rare earths.—The rare earths are separated from other elements by the addition of oxalic acid in 0·5N acid at 60°. The oxalates of the rare earths, of thorium and (partially) that of zirconium precipitate.

Bi(III), Sb(III) can be precipitated under these conditions also.

Concentration limit.—5.10^{-3} g.-ion of rare earths per litre (500 p.p.m.).

Procedure.—To 0·5 ml of solution as low in acidity as possible, add 0·5 ml of N-HCl, and 0·5 ml of 10 per cent oxalic acid (saturated solution). Warm.

CERIUM

$$Ce = 140\cdot1$$

Among the rare earths this is the only element likely to be met with in analysis. It differs from the others mainly by being able to exist in the IV state of oxidation.

Oxidation numbers.—III in the cerous salts; IV in the ceric salts which resemble those of Th(IV), Ti(IV), Zr(IV), Pb(IV), and U(IV).

Ce(III).—**Cerous salts.**—Ce^{3+} is colourless and a weak acid. $Ce(OH)_3$ precipitates above pH 7·1 (0·01M). The solubility of the oxalate and the fluoride in dilute acids is low. CeO_2 is obtained by igniting the oxalate.

Complexes with citrate and tartrate ions, etc., are formed.

Equilibrium constants

$$Ce(OH)_3 \downarrow \rightleftharpoons Ce^{3+} + 3OH^- \quad \ldots \ldots \ldots \ldots \quad 21\cdot8\text{-}22\cdot7$$
$$Ce(C_2O_4)_3 \downarrow \rightleftharpoons 2Ce^{3+} + 3C_2O_4{}^{2-} \quad \ldots \ldots \ldots \quad 22\cdot7$$
$$Ce(C_2O_4)_3 \downarrow \rightleftharpoons Ce(C_2O_4)_2{}^- + C_2O_4{}^{2-}; \quad pk_3 = 0\cdot8; \quad pk_2 = 4\cdot0; \quad pk_1 = 6\cdot5$$
$$CeSO_3{}^+ \rightleftharpoons Ce^{3+} + SO_3{}^{2-} \quad \ldots \ldots \ldots \ldots \quad 8\cdot0$$
$$CePO_4 \downarrow \rightleftharpoons Ce^{3+} + PO_4{}^{3-} \quad \ldots \ldots \ldots \ldots \quad 18\cdot5$$
$$CeP_2O_7{}^- \rightleftharpoons Ce^{3+} + P_2O_7{}^{4-} \quad \ldots \ldots \ldots \ldots \quad 7\cdot1$$
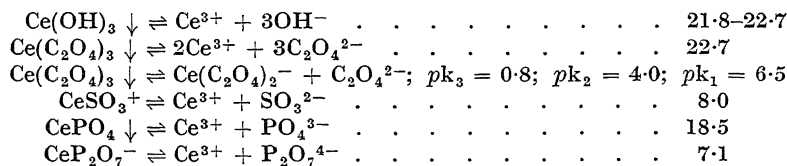
Ce(IV).—Ceric salts.—The yellow $CeOH^{3+}$ and the orange $Ce(OH)_2{}^{2+}$ cations are formed. $Ce(OH)_4$ comes down as a light yellow precipitate at pH $0\cdot8$ ($M\text{-}SO_4{}^{2-}$). The precipitate develops rapidly. Ammonia, caustic soda, salts of weak acids precipitate this hydroxide. After ignition, CeO_2 is very little soluble in HCl, but is soluble in hot concentrated sulphuric acid.

The phosphate is even less soluble than the hydroxide. Complexes are formed with Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$, and $ClO_4{}^-$. Orange complexes are formed with hydrogen peroxide, $Ce(OH)_3.HO_2$; these are stable in neutral or alkaline solution. Very stable tartrate complexes are known.

Ceric oxalate is soluble in an excess of oxalic acid. The complex is gradually destroyed by redox, $Ce_2(C_2O_4)_3$ precipitates.

Equilibrium constants

$$Ce(OH)^{3+} + H_2O \rightleftharpoons Ce(OH)_2{}^{2+} + H^+. \quad \ldots \ldots \quad 0\cdot2$$
$$Ce(OH)_4 \downarrow \rightleftharpoons Ce^{4+} + 4OH^- \quad \ldots \ldots \ldots \quad 54\cdot8$$
$$CeSO_4{}^{2+} \rightleftharpoons Ce^{4+} + SO_4{}^{2-} \quad \ldots \ldots \ldots \quad 3\cdot4$$

Redox

$$Ce \downarrow - 2e \rightleftharpoons Ce^{2+} \quad E_0 = -1\cdot68 \text{ volts}$$
$$Ce^{2+} - e \rightleftharpoons Ce^{3+} \quad E_0 = -1\cdot6 \quad ,,$$
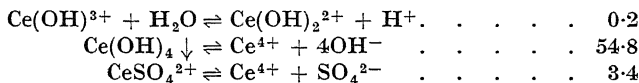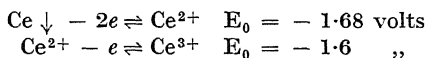
The element is thus not detectable in the II state of oxidation.

$$Ce(OH)^{3+} + H^+ + e \rightleftharpoons Ce^{3+} + H_2O \quad E_0 = 1\cdot71 \text{ volts}$$
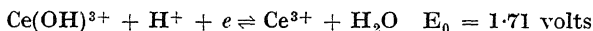
Solution	E'_0 formal (volts)
9N-HClO$_4$	1·90
N-HClO$_4$	1·70
N-HNO$_3$	1·61
M-H$_2$SO$_4$	1·44
N-HCl	1·28

The formal potential is modified by the formation of complexes.

In sulphuric acid the hydroxide $Ce(OH)_4$ precipitates above pH $0\cdot8$ ($0\cdot01M$ solution of a ceric salt), and the oxidizing power then rapidly falls. $Ce(OH)_3$ oxidizes rapidly in the air in alkaline solution yielding $Ce(OH)_4$. In acid solution, Ce^{3+} is oxidized by sodium bismuthate, and by $S_2O_8{}^{2-} + Ag^+$ in the hot. Ce (IV) oxidizes Fe^{2+}, $Fe(CN)_6{}^{4-}$, I^-, H_2S, SO_2, HN_3, $(COOH)_2$, H_2O_2, concentrated HCl, etc.

H_2O_2 reduces Ce(IV) in acid solution to $Ce(OH)_3$. Ignition of $Ce(OH)_3$ in air yields CeO_2.

Detection

(1) **Ferrous o-phenanthroline.**—This is a redox indicator which changes from red to pale blue in strongly oxidizing solution, $1\cdot1$ volts. Only very powerful oxidants, like Ce(IV), are able to make it change colour. Usually, Ce is present as Ce(III), and so must be oxidized at the

start with persulphate in the presence of Ag^+ ions, the excess of persulphate being then destroyed by boiling. Ce(IV) is then detected by its ability to oxidize ferrous *o*-phenanthroline.

Solutions and materials required.—Pure ammonium persulphate (solid).

25 per cent $AgNO_3$ (aqueous).

Ferrous *o*-phenanthroline $10^{-4}M$ obtained by dilution of the normal 0·025M solution prepared thus:

$FeSO_4.7H_2O$ . . . . 0·7 g
o-phenanthroline . . . . . . 1·5 g
Water . . . . 100 ml

Procedure.—Add 1 drop of the silver nitrate to 1 drop of the solution being examined, so as to precipitate any chlorides and still have an excess of silver to catalyse the oxidation with persulphate. If the solution contains much chloride, the major part can conveniently be removed preliminarily by boiling after the addition of 2 drops of sulphuric acid. Add a crystal of persulphate, bring to the boil, and carry on the boiling for a minute to destroy the excess of persulphate. Cool. Add 1 drop of the reagent. The solution will become red if no Ce(IV) is present. If it is present, the reagent is oxidized and becomes colourless.

Concentration limit and interferences.—10^{-4} g.-ion/litre of cerium (15 p.p.m.) can be detected if $10^{-4}M$ ferrous *o*-phenanthroline is used. If the solution contains other coloured ions, the sensitivity decreases and it is then better to use a more concentrated indicator.

The reaction is specific within the rare earth group. Sufficiently powerful oxidants give the same reaction. These are: Mn(VII), V(V) at a concentration above 0·05M.

(2) **N-phenylanthranilic acid**: the procedure is the same.

Solution required.—Sodium N-phenylanthranilate in concentration of about 10 mg/litre.

Procedure.—Carry out the oxidation as in the preceding case in a small test-tube. Finally add 1 drop of the reagent. The solution becomes purple in the presence of Ce(IV).

Concentration limit and interfering substances.—$10^{-4·5}$ g.-ion of Ce^{4+} per litre (5 p.p.m.) can be detected. Strongly coloured ions diminish the sensitivity, and once again it is then a good idea to use more concentrated reagent.

The reaction is specific within the rare earth group.

Sufficiently powerful oxidants give the same reaction. These are: Mn(VII), V(V) at a concentration greater than 10^{-3} and Cr(VI) at above $10^{-1·5}M$; this latter acts slowly (but the reaction is catalysed) by Fe^{3+}, Au(III), conc. HNO_3. The metals of the platinum group interfere.

Detection of cerium in the presence of manganese.—In the presence of manganese it is impossible to detect cerium by oxidation in acid solution; the following method should be used. After oxidizing the alkaline solution with persulphate in order to detect chloride, the solution is centrifuged and separated. The precipitate, which contains

$Ce(OH)_4$, is redissolved in $9N$-H_2SO_4. $Ce(IV)$ is then characterized in this precipitate as shown on page 174.

Concentration limit.—20 p.p.m.

Interfering substances.—The reaction is specific.

Separation of cerium from other rare earths.—The solution is adjusted to have a pH between 1·5 and 6·0, and the cerium is converted to the IV oxidation state. Under these conditions $Ce(OH)_4$ precipitates. However, it can be characterized by the methods already referred to without making any separation.

TITANIUM—ZIRCONIUM—THORIUM

$Ti(IV)$, $Zr(IV)$, $Th(IV)$ have properties fairly close to one another and they resemble $Ce(IV)$, $Si(IV)$, $Sn(IV)$, $Pb(IV)$, $U(IV)$.

IVa	Va
C(IV)	
Si(IV)	
Ti(IV)	
Zr(IV)	Nb(V)
Hf(IV)	Ta(V)
Th(IV)	

The cations are very acid, and colourless. The very low solubility hydroxides exist over a considerable range of pH.

The anions are not of much importance in analysis. The hydroxides age rapidly and become less soluble.

Complexes.—$Ti(IV)$ and $Zr(IV)$ give complexes with Cl^-, SO_4^{2-}, which are fairly stable; those with fluoride and oxalate ions are quite stable. They are thus very similar to $Sn(IV)$. The solubility of ThF_4 is very low, like that of CeF_4 and UF_4. The oxalate complex of thorium is destroyed at pH < 2 and the low-solubility oxalate is thrown down, which is a behaviour similar to that of the rare earths.

$Th(IV)$ has numerous low-solubility compounds.

FIG. 44.—APPARENT SOLUBIL-ITY OF THE HYDROXIDES OF $Ti(IV)$, $Zr(IV)$ AND $Th(IV)$ AS A FUNCTION OF pH

States of oxidation.—In general, there is only one stable one: IV. However, titanium can exist in the III and even the II oxidation state.

TITANIUM

Ti = 47·9

Oxidation number.—II is of little importance. III—in this titanium is similar to $Fe(III)$ and $Al(III)$. IV—compounds of titanium in this state are stable in air.

$Ti(III)$.—Titanous (Ti^{3+}) and titanyl (TiO^+) salts. The cation is violet, and acid, similar to Fe^{3+}. $Ti(OH)_3$, is a violet-black precipitate which comes down at pH's above 3.

Oxalate, tartrate, and thiocyanate, etc., complexes are known.

$$Ti(OH)_3 \downarrow \rightleftharpoons Ti^{3+} + 3OH^- \quad . \quad . \quad . \quad . \quad 35$$
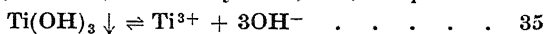
$Ti(IV)$.—Titanic salts.—In N-$HClO_4$ or N-HNO_3, $Ti(IV)$ does not

exist in solution except as a low concentration of $TiOH^+$ and TiO^{2+}. In HCl or H_2SO_4 colourless complexes are form ed. Thewhite hydroxide precipitates in $N-Cl^-$ at pH 0·7(0·01M).

On boiling, the hydroxide ages rapidly and becomes still less soluble. It is very slightly amphoteric. It dissolves in cold potash and slightly in alkali carbonates. In the hot, or on dilution, low-solubility alkali titanates are obtained. These compounds can also be formed by fusion with alkali carbonates. $TiCl_4$ boils at 135° C.

Low-solubility compounds.—$Ti(OH)PO_4$, not much soluble at pH 3. The ferrocyanide, orange-brown. Tannin gives an orange compound of very small solubility.

Complexes.—Very stable citrate and tartrate complexes, from which NH_3 does not precipitate the hydroxide. Low-stability carbonate complexes. There is also a titanicyanide ion $Ti(CN)_6^{2-}$.

Orange complexes are formed with hydrogen peroxide. After attack by molten Na_2O_2 a colourless complex is obtained which turns orange in acid solution. Fluoride complexes, destroyed by prolonged boiling, with oxidants such as MnO_4^-. Phosphate ions do not destroy them (differences from $Zr(IV)$).

$$H_2TiO_3 \rightleftharpoons TiO^{2+} + 2OH^- \quad . \quad . \quad . \quad \sim 30$$

Redox (1) $\quad TiO^+ + 2H^+ + e \rightleftharpoons Ti^{2+} + H_2O$. $\quad - 0·37$ volt

in 0·05N-HCl. Ti^{2+} is oxidized by air.

(2) $\quad TiO(OH)^+ + H^+ + e \rightleftharpoons TiO^+ + H_2O \quad E_0 = 0·03$ volt
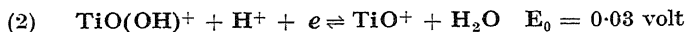
Formal potential: 0·03 volt in N-HCl. The reaction is slow. The system is strongly reducing. Ti(III) salts reduce Fe^{3+}, NO_3^-, ClO_3^-, ClO_4^- in the hot. They oxidize rapidly in the air. Ti(IV) salts are reduced by hydrosulphites, by Zn, Cd, Sn, in acid solution, but not by SO_3^{2-} or H_2S.

Detection

Hydrogen peroxide.—In acid or neutral solution, hydrogen peroxide gives orange-coloured complexes.

Solution required.—5 vol. H_2O_2.

Procedure.—Add a drop of the H_2O_2 to a drop of the solution.

Concentration limit.—5.10^{-4} g.-ion of Ti per litre (or 30 p.p.m.).

Interfering substances.—(1) In alkaline solution the orange colour disappears, as a result of the formation of colourless complexes.

(2) Powerful oxidants like Ce(IV) in acid solution oxidize H_2O_2, whence the need for an excess. The same thing applies with powerful reductants. Fe^{2+} is oxidized to Fe^{3+} by hydrogen peroxide, causing a change of colour of the same kind, but weaker. Much Fe^{3+} can interfere on account of its own colour. In these cases, add 1 or 2 drops of phosphoric acid to complex the Fe^{3+}.

(3) A certain number of ions give weak yellow to orange colorations: Nb(V), Mo(VI), W(VI), etc.

V(IV) and V(V) give a coloration which is similar and just as intense.

Detection of titanium in the presence of vanadium.—Titanium can be precipitated in very dilute acid as the arsenate, in the presence of

zirconium which induces the precipitation. In this manner it is separated from all the interfering ions, and the reaction with hydrogen peroxide can then be carried out on the precipitate.

Solutions required.—1 per cent aqueous solution of zirconyl chloride free from titanium.

Arsenic acid . . . . . 20 per cent aqueous solution
4N-HCl

Procedure.—To 5 drops of the solution add 1 drop of 4N-HCl, then 1 drop of arsenic acid and 1 drop of Zr(IV). Boil. Centrifuge. Wash twice by centrifuging with 2 drops of water, 1 drop of 4N-HCl and 1 drop of arsenic acid. Take up the precipitate with 1 drop of $4N-H_2SO_4$. With a pipette, transfer to a test plate and add 1 drop of hydrogen peroxide.

An orange coloration which disappears when fluoride is added indicates the presence of titanium.

ZIRCONIUM

$Zr = 91\cdot2$

Oxidation number.—IV.

Influence of pH.—Colourless cations: Zr^{4+} in $> 2N-HClO_4$, $Zr(OH)^{3+}$ up to pH $0\cdot7$, thereafter $Zr(OH)_2^{2+}$.

At pH 2 ($0\cdot01M$) in HCl the white $Zr(OH)_4$ precipitates. It can remain in colloidal solution. It is practically insoluble in alkaline solution. Low-solubility alkali zirconates do exist; they are destroyed by heat. The hydroxide develops and its solubility becomes extremely low in the process, even in concentrated HCl.

Low-solubility compounds.—These are numerous: the phosphate $ZrH_2(PO_4)_2$, the arsenate, the compounds with arsonic acids are all of low solubility in dilute acids. $Zr(IO_3)_2$ is soluble in hot dilute HCl.

Complexes.—ZrO^{2+} and Zr^{4+} give numerous complexes: sulphate, relatively stable, chloride rather unstable, fluoride and oxalate very stable (difference from Th(IV) and Ce(IV) of which the corresponding compounds precipitate in dilute acid). With CO_3^{2-} very unstable complexes are formed. After attack by molten Na_2CO_3, ZrO_2 remains insoluble after boiling.

A white complex Zr_2O_7 is formed with hydrogen peroxide. This is of low solubility in dilute acid; complexes are formed which are soluble in alkalis. Complexes are also formed with polyalcohols.

Equilibrium constants

$$ZrOH^{3+} + H_2O \rightleftharpoons Zr(OH)_2^{2+} + H^+ \quad \dots \quad 0\cdot7 \; (I = 2)$$
$$H_2ZrO_3 \downarrow \rightleftharpoons ZrO^{2+} + 2OH^- \quad \dots \quad \sim 26$$
$$H_2ZrO_3 \downarrow \rightleftharpoons HZrO_3^- + H^+ \quad \dots \quad \sim 18$$
$$Zr(SO_4)_3^{2-} + H^+ \rightleftharpoons Zr(SO_4)_2 + HSO_4^- \quad \dots \quad 0\cdot0$$
$$Zr(SO_4)_2 + H^+ \rightleftharpoons ZrSO_4^{2+} + HSO_4^- \quad \dots \quad 1\cdot7$$
$$ZrSO_4^{2+} + H^+ \rightleftharpoons Zr^{4+} + HSO_4^- \quad \dots \quad 2\cdot7$$
$$ZrF_3^+ \rightleftharpoons ZrF_2^{2+} + F^-; \quad pk_3 = 6\cdot0; \quad pk_2 = 7\cdot5; \quad pk_1 = 9\cdot0$$
$$ZrCl^{3+} \rightleftharpoons Zr^{4+} + Cl^- \quad \dots \quad 0\cdot3$$
$$ZrNO_3^{3+} \rightleftharpoons Zr^{4+} + NO_3^- \quad \dots \quad 0\cdot3$$

Detection

Alizarin.—Zirconium hydroxide gives, with numerous reagents, adsorption compounds which are coloured or fluorescent, and stable in dilute acid, enabling the reaction to be made selective or even specific. Alizarin S and alizarin give red colorations in strong acid.

Solution required.—N/1000 aqueous alizarin S.

Procedure.—Add 1 drop of reagent to 1 drop of solution, strongly acidified with HCl.

Concentration limit.—10^{-3}–10^{-4} g.-ion/litre of Zr (10–100 p.p.m.).

Interfering substances.—(1) The majority of ions which give a similar reaction do not react in strongly acid solution.

In a solution which is not very strongly acid, Ti(IV) gives an orange-red coloration. Even in conc. HCl, Ti(IV) gives an orange coloration in 0·1 g.-ion/litre concentration, but at 0·01 concentration, there is no longer any coloration. If much Ti(IV) is present, it is therefore advisable to dilute the solution suitably with conc. HCl. When the HCl concentration is high enough, Th(IV) no longer interferes.

(2) Powerful oxidants destroy the coloration.

(3) SO_4^{2-}, which slightly complexes Zr(IV), diminishes the sensitivity. Ions noted for their ability to form complexes, such as F^- and $C_2O_4^{2-}$, should not be present.

(4) Ions which precipitate Zr(IV): phosphates, arsenates, etc., interfere. Co^{2+} intrudes its own colour and so interferes. Sb(III), Mo(VI), W(VI) interfere.

Morin.—This reagent gives a green fluorescence even in 10N-HCl (see Al, p. 158).

Solutions required.—0·001 per cent solution of morin in alcohol. 12N-HCl.

Procedure.—To 1 drop of solution, add 1 drop of reagent and 5 drops of the concentrated acid. Examine in U.V. light.

Concentration limit.—About 10^{-4} g.-ion/litre (10 p.p.m.).

Interfering substances.—No other ion gives a fluorescence under these conditions. The fluorescence is inhibited by ions which are coloured red and yellow in 10N-HCl, and also by those which oxidize the reagent: Cu^{2+}, Fe^{3+}, V(V) and Cr(VI), the precious metals, gold and the platinum group metals. SO_4^{2-} diminishes the sensitivity. H_3PO_4 interferes by precipitation of Zr(IV). Th(IV), Sb(III), Sb(V) give a brown coloration which gradually disappears. Ce(IV) is reduced by H_2O_2 and does not interfere. Sn(IV) gives no reaction in hot 2H-NCl.

Zirconium gives compounds which are of low solubility in very weak acid: phosphates, arsenates, phenylarsonates. The azophenylarsonic derivatives are coloured, and the reaction is then very sensitive.

p-Dimethylaminoazophenylarsonic acid.—A red-brown precipitate is obtained with Zr(IV), even in 2N-HCl.

Solution required.—2 per cent solution of the above acid in 10N-HCl.

Procedure.—To 1 drop of reagent add 1 drop of the test solution.

Concentration limit.—2.10^{-4} g.-ion/litre (20 p.p.m.).

13

Interfering substances.—Ti(IV), Mo(VI) give an analogous reaction, but, in the presence of concentrated hydrogen peroxide (1 drop of 100 vol.), complexes are produced of sufficient stability to inhibit the reaction.

Titanium and zirconium in the course of analysis.—At the commencement of an analysis, ZrO_2 and TiO_2 are frequently left behind along with SiO_2 among the insolubles. They are then insoluble in 3–4N-HCl. If they are treated with 2N-HCl, they can partially dissolve. The fresh hydroxides are soluble in $H_2SO_4 > 2N$. The best procedure for getting them into solution is to attack them with fused $K_2S_2O_7$ and to extract the fused mass with 9N-H_2SO_4 in the cold (see p. 340). From natural products, ZrO_2 is more easily brought into solution by attack with a mixture of 3·4 g of $Na_2CO_3 + K_2CO_3$ and 2·3 g of borax. Boil with 10 per cent NaOH, and filter. Take up with 12N-H_2SO_4 and H_2O_2. Carry out the test for zirconium by adding phosphate.

HAFNIUM

Hf = 178·6

Very similar to zirconium, which it always accompanies, though in small quantities (1–2·5 per cent).

THORIUM

Th = 232·1

State of oxidation.—IV.

Hydroxide.—White $Th(OH)_4$ or H_2ThO_3, colloidal. It commences to precipitate at pH 3 (0·01M). The precipitation is total at around pH 6·0. Th^{4+} is colourless.

Salts of low solubility in acid solution.—The double sulphate with K^+. The oxalate is of low solubility in strong acid (similarity with the rare earths). ThF_4 or $Th(ThF_8)$, $Th(IO_3)_2$ have low solubility in dilute HNO_3. The hypophosphate ThP_2O_6 is of low solubility in conc. HCl. ThP_2O_7, $Th(Fe(CN)_6)$ are of low solubility in dilute acid. The phosphate precipitates at pH 2·7: $Th_3(PO_4)_4$.

Complexes.—With oxalate ion: the complex is destroyed in dilute acid, the oxalate itself being reprecipitated. The oxalate is thus soluble in solutions of the alkali oxalates—a reaction similar to that with Zr^{4+}, but this latter complex is not destroyed by acids (separation of Zr—Th—rare earths). Complexes are formed with hydroxylated organic acids. $Th(CO_3)^{6-}$ is not precipitated by ammonia. With H_2O_2, a complex which has a low solubility in acids is formed.

Equilibrium constants

$$Th(OH)_4 \downarrow \rightleftharpoons Th^{4+} + 4OH^- \quad . \quad . \quad . \quad . \quad . \quad 46$$
$$ThNO_3^{3+} \rightleftharpoons Th^{4+} + NO_3^- \quad . \quad . \quad . \quad . \quad . \quad 0·7 \ (I = 0·5)$$
$$ThCl^{3+} \rightleftharpoons Th^{4+} + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 0·25 \ (I = 0·5)$$
$$ThF_4 \downarrow \rightleftharpoons Th^{4+} + 4F^- \quad . \quad . \quad . \quad . \quad . \quad 28·1; \ 27·4 \text{ for } I = 0·5$$
$$ThF_3^+ \rightleftharpoons ThF_2^{2+} + F^-; \ pk_3 = 4·7; \ pk_2 = 6·1; \ pk_1 = 7·8 \ (I = 0·5)$$
$$Th(IO_3)_4 \downarrow \rightleftharpoons Th^{4+} + 4IO_3^- \quad . \quad . \quad . \quad . \quad . \quad 14·6 \ (I = 0·5)$$
$$Th(IO_3)_4 \downarrow \rightleftharpoons Th(IO_3)_3^+ + IO_3^- \quad . \quad . \quad . \quad . \quad 7·5$$

NIOBIUM (COLUMBIUM) AND TANTALUM

Nb = 92·9; Ta = 180·9

State of oxidation.—V is the basic one. Nb(III) compounds are known. The elements are very similar to one another, and are rather hard to separate because they have no marked chemical characteristics.

Hydroxides.—These are of low solubility at any rate over the range pH 0–14, but they can remain at least partially in colloidal solution under many conditions. The presence of other hydroxides which easily become colloidal, mainly those of Ti(IV) and Si(IV), favours their conversion to the colloidal condition; NH_3 and NH_4^+ can flocculate them, as also can gelatine at the boil.

Complexes.—Nb(V) and Ta(V) are thus present in solution almost entirely in the state of complexes—fluorides, oxyfluorides, tartrates, oxalates, those with hydrogen peroxide, CNS^-, poly-alcohols, etc. The oxalate complexes of Nb(V) are more stable than those of Ta(V); tantalum hydroxide partially precipitates in ammonia (difference from Nb). Tannin totally precipitates tantalum at pH 4 in oxalic acid solution as a yellow compound; niobium (orange precipitate) comes down at pH 4–6. The tartrate complexes are more stable.

FIG. 45.—APPARENT SOLUBIL-ITY OF Nb(V) AND Ta(V) AS A FUNCTION OF pH

Low-solubility compounds.—Cupferron, and arsonic acids, pre-cipitate Nb(V) and Ta(V) in dilute acid, the first even in the presence of tartrate ions.

Redox.—(1) The metals are not attacked by strong acids and not even by aqua regia (passive). Tantalum is attacked by HF with the formation of complexes.

(2) $NbO^{3+} + 2H^+ + 2e \rightleftharpoons Nb^{3+} + H_2O$ $E_0 = -0.34$ volt

Nb^{3+} is blue-black.

URANIUM

U = 238·1

Uranium differs from the other elements of the ammonia group. Some of its compounds are less soluble than the hydroxide, in particular the sulphide.

States of oxidation.—III, IV in which U is similar to Th(IV); in the V state there is almost complete disproportionation. The uranyl salts and the uranates contain U(VI). U is most frequently encountered in this latter state.

U(III).—U^{3+} cations are pinkish-purple. $U(OH)_3$ is brown.

U(III) is oxidized rapidly in the air.

U(IV)

The uranous cations are green, (U^{4+}). In weak acid solution, basic cations UOH^{3+} are formed which polymerize slowly. Fairly stable in the air. $U(OH)_4$ is green.

Low-solubility compounds and complexes are similar to those of Th(IV). UF_4 has a low solubility in dilute mineral acid; the same is true of the oxalate and the phosphate; phosphate and oxalate complexes are formed in less acid solution.

Equilibrium constants

$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$ . . . . . . 1·5 (I = 0·5); 0·7 (I = 0)

$UCl^{3+} \rightleftharpoons U^{4+} + Cl^-$ . . . . − 0·8 for I = 0

U(V).—UO_2^+ is not very stable. It disproportionates into U(IV) and U(VI). In alkaline solution it yields anions.

$UO_2^+ + H_2O \rightleftharpoons UO_2OH + H^+$ 8

$2UO_2^+ + 4H^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 2H_2O$ . . − 6
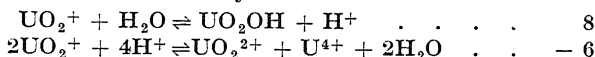
U(VI)

In acid solution, the UO_2^{2+} cations are present. At pH 2–3 various condensed basic ions are formed. The hydroxide precipitates above pH 3·8; the precipitation becomes practically quantitative at pH 5·3. The hydroxide can remain in colloidal solution up to pH 7. UO_3 is orange. The cations UO_2^{2+}, UO_2OH^+, and $UO_2NO_3^+$ are yellow with a green fluorescence.

The precipitation of the hydroxide is, in general, accompanied by the precipitation of yellow alkali uranates and polyuranates of low solubility: Na_2UO_4, $Na_2U_2O_7$, etc. When a uranyl salt is neutralized in solution, in general a yellow precipitate of an alkali uranate is formed.

Complexes.—Soluble orange anions are formed with hydrogen peroxide; $UO_4.2H_2O_2$ is not very soluble, but dissolves in strong acid solution. Low-stability oxalate complexes are formed, and stable citrate and tartrate ones; the low-stability fluoride and carbonate complexes are destroyed at $pH < 7$ or > 12. Fairly stable complexes with V(V) are known.

Low-solubility compounds.—The brown sulphide, UO_2S, is soluble in dilute acid. The yellow phosphate does not dissolve appreciably at pH 2. The solubility of the brownish-red uranyl ferrocyanide is very low.

Equilibrium constants

$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$ . . . . 4·8

$2UO_2^{2+} + H_2O \rightleftharpoons (UO_2)_2OH^{3+} + H^+$ . . . 2·5

$UO_2Cl^+ \rightleftharpoons UO_2^{2+} + Cl^-$ . . . . . . − 0·4 (I = 0)

$UO_2SO_4 + H^+ \rightleftharpoons UO_2^{2+} + HSO_4^-$ . . . . − 0·7

$UO_2NO_3^+ \rightleftharpoons UO_2^{2+} + NO_3^-$ . . . . + 0·7; 0·6 for I = 7

$UO_2(C_2O_4)_2^{2-} \rightleftharpoons UO_2C_2O_4 + C_2O_4^{2-}$ . . . 1·1

$UO_2(C_2O_4) \downarrow \rightleftharpoons UO_2^{2+} + C_2O_4^{2-}$ . . . . 5·8

Redox

(1) $\quad U \downarrow - 3e \rightleftharpoons U^{3+} \quad E_0 = -1·7$ volt

(2) $\quad U^{3+} - e \rightleftharpoons U^{4+} \quad E_0 = -0·63$ volt
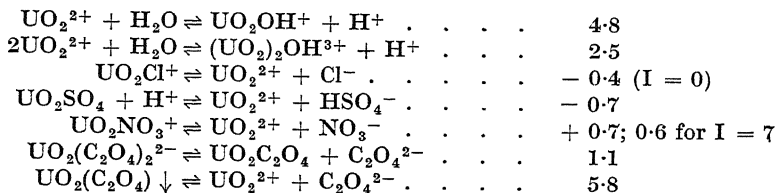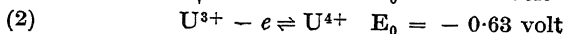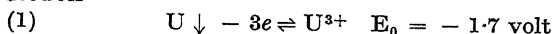
Practically the same values apply for the formal potentials in N-HClO$_4$ and N-HCl; $-$ 0·85 volt in N-H$_2$SO$_4$. The exchange of electrons is in general rapid in both directions. U^{3+} is a strong reductant and oxidizes rapidly in air to U^{4+}. The hydroxide U(OH)$_3$ reduces H$^+$.

U^{4+} is partially reduced to U^{3+} by powerful reductants like zinc, zinc amalgam, etc.; H$^+$ is reduced at the same time.

$$(3) \qquad \frac{\begin{aligned} U^{4+} + 4H_2O - e &\rightleftharpoons UO_2^+ + 4H^+ \qquad \text{slow} \\ UO_2^+ - e &\rightleftharpoons UO_2^{2+} \qquad\qquad\quad \text{rapid} \end{aligned}}{U^{4+} + 4H_2O - 2e \rightleftharpoons UO_2^{2+} + 4H^+}$$
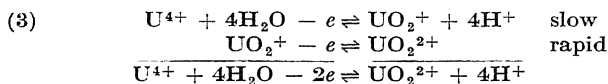
Electron exchange is in general slow. E$_0$ = 0·31 volt. U^{4+} is fairly stable in air. It is oxidized by I$_2$, Fe^{3+}, and powerful oxidizing agents.

Detection

Ferrocyanide.—Brown uranyl ferrocyanide is precipitated.

Solution required.—Potassium ferrocyanide, 10 per cent.

Procedure.—Add 1 drop of the reagent to 1 drop of the solution on a test plate.

Concentration limit.—5.10^{-4} g.-ion of UO$_2^{2+}$ per litre (100 p.p.m.).

Interfering substances.—Numerous ions give coloured ferrocyanides of low solubility. The most troublesome are Fe^{3+}, which gives prussian blue, and Cu^{2+}, which also gives a brown ferrocyanide. These should be reduced before carrying out the test by the addition of a drop of 15 per cent iodide, then a drop of thiosulphate (15 per cent) in order to remove the iodine liberated.

In the majority of cases, it is necessary to separate a large number of ions by neutralization, followed by the addition of carbonate in excess, whereby the uranium is kept in solution as a carbonate complex. To 1 drop of solution, add 3 drops of sodium carbonate (20 per cent) and boil for a minute. Centrifuge. Remove 1 drop of the solution. Add 1 drop of 4N-HCl to it and proceed as before. The sensitivity may then be very much smaller.

Mo(VI) and Ti(IV) give brown precipitates.

Remarks about reactions with ferrocyanide.—Nearly all the ferrocyanides are of low solubility: Fe(III) blue; Cu(II) brown; Pb(II) white; Th(IV) white; Ni(II) green; Co(II) greyish green; Zn(II) white; Mn(II) white; Cd(II) white; VO$_2^{2+}$ green; Ag$^+$ white; Hg^{2+} white; Hg$_2^{2+}$ white.

TRANSURANIUM ELEMENTS

These are: Neptunium Np, Plutonium Pu, Americium Am, Curium Cm, Berkelium Bk, Californium Cf. They are very similar to Uranium, and form a homogeneous group with it.

At pH = 0 the cations MO$_2^{2+}$, MO^{2+}, M^{4+}, M^{3+}

are formed from neptunium and plutonium.

GALLIUM—INDIUM—THALLIUM

Ga = 69·7; In = 114·8; Tl = 204·4

They are allied to the ammonia group by the properties of their trivalent hydroxides, but are distinguished from it in particular by the properties of their sulphides.

They appear in column III*b* of the periodic classification and have sulphides of low solubility, like the majority of elements in the *b* subgroups.

Thallium will be studied with silver, which it resembles when its oxidation number is I.

$\longrightarrow$

II*b*	III*b*	IV*b*
Zn(II)	Ga(III)	Ge(IV)
Cd(II)	In(III)	Sn(IV)
Hg(II)	Tl(III)	Pb(IV)

The cations increase in acidity in the direction of the arrow. Tl^{3+} is acid, more so than Hg^{2+} and less so than Pb^{4+}.

$Tl(OH)_3$, of very low solubility, is not amphoteric.

In^{3+}, more acid than Cd^{2+} which it resembles, has an amphoteric hydroxide.

Ga^{3+}, more acid than In^{3+}, lies between Zn^{2+} and Ge^{4+}; all three yield anions. Ga^{3+} is analogous to Zn^{2+}.

In the vertical direction, the rule does not apply: Tl^{3+} is the most acid of the three.

Notes.—The analogies are more marked between Zn(II) and Cd(II)— Ga(III) and In(III)—Ge(IV) and Sn(IV)

Oxidation state I+

III*b*	IV*b*
In(I)	Sn(II)
Ga(I)	Ge(II)
Tl(I)	Pb(II)

Same rules as before. Tl^+ is neutral and resembles the alkalis. Pb^{2+} is not very acid.

Redox

$\longrightarrow$

Zn^{2+}/Zn ↓	Ga^{3+}/Ga^+	Ge^{4+}/Ge^{2+}
− 0·76 volt		
Cd^{2+}/Cd ↓	In^{3+}/In^+	Sn^{4+}/Sn^{2+}
− 0·40 volt		+ 0·15 volt
Hg^{2+}/Hg ↓	Tl^{3+}/Tl^+	Pb^{4+}/Pb^{2+}
+ 0·85 volt	+ 1·28 volts	+ 1·75 volts

The potential increases in the direction of the arrows.

GALLIUM

Similar to Al^{3+} and also to Zn^{2+}.

Oxidation numbers.—III in solution; anhydrous compounds in which it is II and I are known. The metal melts at 29° C.

Ga^{3+} is a colourless cation. The white hydroxide precipitates at pH 2·5 (0·01M) and redissolves, when it is not in the aged condition, at about pH 9·7, thus in ammonia and also ammonium carbonate. Boiling precipitates it in a less soluble form.

In fairly concentrated solution, basic salts precipitate.

The ferrocyanide is white, and its solubility is low. Ga_2S_3 is of low solubility, and easily transforms into $Ga(OH)_3$. $GaCl_3$ is volatile above 200°.

$Ga(III)$ can be extracted by ether from fairly concentrated HCl. Gallium oxinate is extracted by chloroform above pH 2·0. The chloroform solution is fluorescent.

Equilibrium constants

$$Ga^{3+} + H_2O \rightleftharpoons GaOH^{2+} + H^+ \quad . \quad . \quad . \quad . \quad 2\cdot6\text{--}4\cdot6$$
$$GaOH^{2+} \rightleftharpoons GaO^+ + H^+ \quad . \quad . \quad . \quad . \quad . \quad 3\cdot2$$
$$Ga(OH)_3\downarrow \rightleftharpoons Ga^{3+} + 3OH^- \quad . \quad . \quad . \quad . \quad 35\text{--}36\cdot5$$
$$Ga(OH)_3\downarrow \rightleftharpoons H_2GaO_3^- + H^+ \quad . \quad . \quad . \quad 11\cdot7\text{--}15$$
$$H_2GaO_3^- \rightleftharpoons HGaO_3^{2-} + H^+ \quad . \quad . \quad . \quad . \quad 10\cdot3$$
$$HGaO_3^{2-} \rightleftharpoons GaO_3^{2-} + H^+ \quad . \quad . \quad . \quad . \quad 11\cdot7$$
$$Ga\ oxine_3\downarrow \rightleftharpoons Ga^{3+} + 3\ oxine^- \quad . \quad . \quad . \quad 40\cdot8$$

Redox

$$Ga^{3+} + 3e \rightleftharpoons Ga\downarrow \quad E_0 - 0\cdot52\ \text{to} - 0\cdot69\ \text{volt}$$
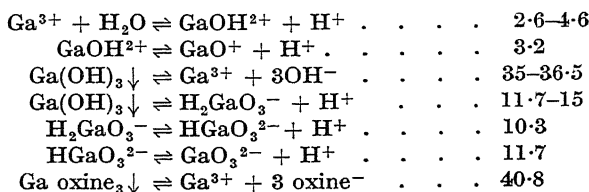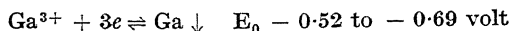
Detection of gallium.—(1) Chrome blue (see p. 158) gives a sensitive and selective reaction. For the characterization of Ga in the presence of Al^{3+} the separation can be effected either with ether from HCl, or by extracting the oxinate with chloroform.
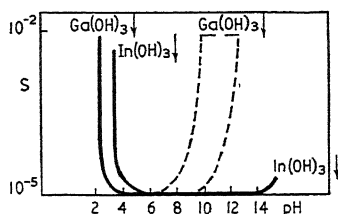
FIG. 46.—APPARENT SOLUBILITY OF $Ga(III)$ AND $In(III)$ HYDROXIDES AS A FUNCTION OF pH

(2) Gallium oxinate in chloroform solution is fluorescent. Compounds of Fe(III) and V with oxine interfere, and these elements must be separated beforehand.

The problem, which is in general to detect traces of Ga^{3+} in the presence of Al^{3+}, involves the determination of traces of Ga^{3+}, and is dealt with in quantitative analysis.

(3) **Violet coloration of the flame.**—The visible spectrum has lines at 403 and 417 mμ.

INDIUM

Similar to Al^{3+} and Cd^{2+}. Same states of oxidation as gallium. The metal melts at 145°.

In^{3+} is colourless. White $In(OH)_3$ precipitates above pH 3·4 (0·01M) and redissolves above pH 14, provided that it has not developed.

In concentrated solution basic salts precipitate.

Oxalate complexes $In(C_2O_4)_2^-$ and $KIn(C_2O_4)_2$ of rather low solubility are formed. The fluoride InF_3 dissolves to the extent of 0·5M and the complex Na_3InF_6 to the extent of 0·35M; $InOF$ is of rather low solubility.

In_2S_3, pale yellow to orange, is soluble in the hot in the presence of S^{2-}. It precipitates at pH 2–3. In alkaline solution, a white precipitate is obtained.

Equilibrium constants

$$In^{3+} + H_2O \rightleftharpoons InOH^{2+} + H^+ \quad . \quad . \quad . \quad . \quad . \quad 3·7$$
$$In(OH)_3 \downarrow \rightleftharpoons In^{3+} + 3OH^- \quad . \quad . \quad . \quad . \quad . \quad 33·9$$
$$In(OH)_3 \downarrow \rightleftharpoons H_2InO_3^- + H^+ \quad . \quad . \quad . \quad \sim 16$$
$$In(IO_3)_2 \downarrow \rightleftharpoons In^{3+} + 2IO_3^- \quad . \quad . \quad . \quad . \quad 10·6$$
$$In(oxine)_3 \downarrow \rightleftharpoons In^{3+} + 3 \text{ oxine}^- \quad . \quad . \quad . \quad 36·7$$
$$In(C_2O_4)_2^- \rightleftharpoons In^{3+} + 2C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad 8·6$$
$$KIn(C_2O_4)_2 \downarrow \rightleftharpoons In(C_2O_4)_2^- + K^+ \quad . \quad . \quad . \quad 4·4$$

Redox

$$In^{3+} + 3e \rightleftharpoons In \downarrow \quad E_0 = -0·34 \text{ volt slow}$$
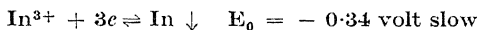
Formal potentials

N-HCl, M-InCl$_3$ $E = -0·3$ volt
N-KOH $E = -0·8$ „
M-Na$_2$CO$_3$ $E = -0·47$ „

Visible spectrum.—Blue flame coloration.

Separation from zinc.—Zn mercurithiocyanate is of low solubility, in contrast with Ga^{3+} and In^{3+}.

ZINC GROUP

MANGANESE. NICKEL. COBALT. ZINC. CADMIUM. COPPER

GENERAL PROPERTIES

Cations (II).—Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}. Hydroxides all soluble in a mixture of ammonia and ammonium chloride as a result of the formation of complexes with NH_3. With NaOH, basic salts are in general first obtained, then the hydroxides. The solubility of the sulphides in ammoniacal solution is in general low.

In contrast with the ammonia group, numerous compounds are less soluble than the hydroxide, in particular the sulphides (*b* columns of the periodic classification).

Numerous complexes, but in general rather unstable, except those with CN^-.

The elements in general have several states of oxidation. Fe^{2+}, Cr^{2+} are similar to this group, while Cu^{2+} resembles Pb^{2+}, Hg^{2+}, Mn^{2+}, and Mg^{2+}.

General reagents. — Mercurithiocyanates. — The mercurithiocyanates $M[Hg(CNS)_4]$ are of low solubility and crystallize together, yielding mixed crystals which are often coloured.

With Zn(II), white precipitate for | Zn^{2+} | $\geqslant 10^{-3}$ g.-ion/litre
With Co(II), deep blue precipitate for | Co^{2+} | $\geqslant 5.10^{-3}$,,   ,,
With Cu(II), green precipitate for | Cu^{2+} | $\geqslant 5.10^{-2}$,,   ,,
With Cd(II), white precipitate for | Cd^{2+} | $\geqslant 0.5$,,   ,,

Ni^{2+}, Mn^{2+}, Fe^{2+} do not precipitate.

Thus only two ions, Cu^{2+} and Co^{2+}, give coloured precipitates.

(*a*) **Precipitates with Cu^{2+}.**—*In the presence of Zn^{2+}*, the colour of the mixed crystals varies with the ratio Zn^{2+}/Cu^{2+} as follows:

	White	Mauve	Violet	Black	Deep green	Green
Zn/Cu . .	> 10	10		1	1/10	< 1/10

This is for concentrations of | Cu^{2+} | $\geqslant 10^{-4}$ and | Zn^{2+} | $\geqslant 5.10^{-4}$.

In the presence of Cd^{2+} mixed crystals are obtained only when | Cd^{2+} | $\geqslant 0.5$, which are black for | Cu^{2+} | $= 10^{-1}$, then violet and mauve at lower copper concentrations.

In the presence of Ni^{2+}: for | Ni^{2+} | $\geqslant 10^{-1}$ and | Cu^{2+} | $\geqslant 10^{-1}$ black precipitates can be obtained.

In the presence of Mn^{2+}: when | Cu^{2+} | $\geqslant 10^{-1}$ and | Mn^{2+} | > 1 black precipitates can be obtained.

In the presence of Co^{2+}

	Deep blue	Black	Green
$|\,Co\,|^{2+}/\,|\,Cu^{2+}\,|$	10	1	

for $|\,Co^{2+}\,| \geqslant 5.10^{-3}$ and $|\,Cu^{2+}\,| \geqslant 10^{-2}$.

(*b*) **Precipitates with Co^{2+}.**—In the presence of Zn^{2+}

	White	Pale blue	Blue	Deep blue
$Zn^{2+}\,|\,/\,|\,Co^{2+}\,|$	100	1		1/10

for $|\,Zn^{2+}\,| \geqslant 10^{-3}$ and $|\,Co^{2+}\,| \geqslant 5.10^{-4}$.

In the presence of Cd^{2+}: the same colours, but for $|\,Cd^{2+}\,| \geqslant 0.5$ and $|\,Co^{2+}\,| \geqslant 5.10^{-3}$.

(*c*) **Cu^+, pale yellow precipitate.**—Fe^{2+} in the presence of F^- can reduce Cu^{2+} to Cu^+.

Note.—In the presence of Fe(III) the precipitates take on a pale violet colour.

Precipitation pH's

Hydroxides

	$10^{-2}M$	$10^{-5}M$
Fe^{2+}	5·8	7·3
Zn^{2+}	6·8	8·3
Cd^{2+}	8·3	9·8
Cu^{2+}	5·0	6·5
Mn^{2+}	8·3	9·8
Ni^{2+}	7·2	8·7
Co^{2+}	7·5	9·0

MANGANESE
Mn = 54·9

Oxidation numbers.—All from I to VII.

The stability of the different anions and cations of manganese has been mentioned on page 129. The stable ions and compounds are thus (not mentioning complexes here): Mn^{2+}, $Mn(OH)_2$ (not stable, oxidizes in the air), H_2MnO_3, MnO_4^-; MnO_4^{2-} (only exists in alkaline solution).

Mn(I).—Only exists as a solid complex $K_5Mn(CN)_6$.

Mn(II)

The manganous compounds are similar to those of Fe^{2+}, Ni^{2+}, Co^{2+}.

Influence of pH.—The cation Mn^{2+} is pale pink. White $Mn(OH)_2$ precipitates from pH 8·3 (0·01M). It only dissolves again to an extremely small extent in very strong alkali, yielding $HMnO_2^-$. It does not precipitate at all in the presence of NH_3 (ammines formed). It oxidizes in the air, going brown.

Complexes.—There are numerous complexes of low stability— phosphate, oxalate, ammine, and complexes with hydroxylated organic

compounds. The cyanide complexes are green and more stable, as also are the fluoride complexes.
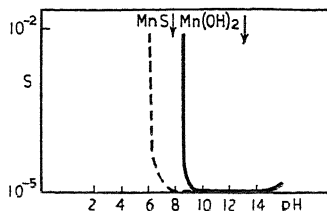
FIG. 47.—APPARENT SOLUBILITY OF THE SULPHIDE AND
HYDROXIDE OF Mn(II) AS A FUNCTION OF pH

Low-solubility compounds.—There are a great number, and their solubility is rarely extremely low. The sulphide MnS is the least soluble; it is salmon pink, oxidizing in the air to MnO_2,aq.; on boiling in the presence of an excess of ammonium sulphide, the less hydrated green sulphide can be obtained. $Mn(NH_4)PO_4$ is a compound of low solubility.

Equilibrium constants

$$Mn(C_2O_4)_3{}^{4-} \rightleftharpoons Mn(C_2O_4)_2{}^{2-} + C_2O_4{}^{2-} \quad . \quad 2\cdot4$$
$$MnC_2O_4 \downarrow \rightleftharpoons Mn^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad 4\cdot4$$
$$Mn(IO_3)_2 \downarrow \rightleftharpoons Mn^{2+} + 2IO_3{}^{-} \quad . \quad . \quad . \quad 6\cdot3$$
$$MnCO_3 \downarrow \rightleftharpoons Mn^{2+} + CO_3{}^{2-} \quad . \quad . \quad . \quad 10\cdot1$$
$$Mn(OH)_2 \downarrow \rightleftharpoons Mn^{2+} + 2OH^- \quad . \quad . \quad . \quad 13\cdot4\text{--}13\cdot1$$
$$Mn(OH)_2 \downarrow \rightleftharpoons HMnO_2{}^{-} + H^+ \quad . \quad . \quad . \quad 19$$
$$MnS \text{ pink} \downarrow \rightleftharpoons Mn^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad 14\cdot9\text{--}15\cdot2$$
$$MnS \text{ green} \downarrow \rightleftharpoons Mn^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad 22\cdot0$$
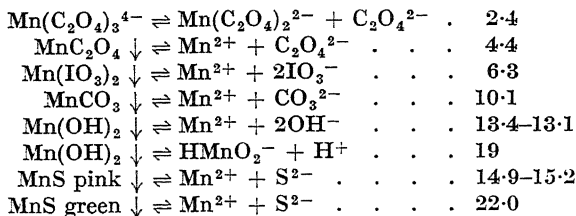
Mn(III)

Manganic compounds.—Mn^{3+} does not exist. Mn_2O_3,aq., brownish black, is very slightly soluble in strong alkali. In acids it disproportionates into Mn^{2+} and MnO_2,aq.

Complexes.—Chloride complexes are brownish black, phosphate ones are violet, sulphate ones are deep red. $Mn(CN)_6{}^{3-}$ is deep red; oxalates $MnC_2O_4{}^+$, $Mn(C_2O_4)_2{}^-$, $Mn(C_2O_4)_3{}^{3-}$ are reddish black, $MnF_5{}^{2-}$ is deep red, $Mn(CH_3COO)_3$ is brown. There are numerous other metaphosphate and pyrophosphate complexes, etc.

Mn(IV)

The cation, a strong acid, is completely hydrolysed by water.

MnO_2,aq. is brown or black. There are deep red chloride complexes $MnCl_6{}^{2-}$, and fluoride analogues, $MnF_6{}^{2-}$, which are yellow. $Mn(CN)_8{}^{4-}$ is a very stable anion.

$$Mn(OH)_4 \downarrow \rightleftharpoons Mn^{4+} + 4OH^- \quad . \quad . \quad . \quad . \quad 56$$
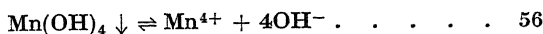
Mn(V).—$MnO_4{}^{3-}$, blue in molten caustic soda, has been described. It disproportionates in any less alkaline environment:

$$2MnO_4{}^{3-} + 4H^+ \rightleftharpoons MnO_4{}^{2-} + MnO_2 \downarrow + 2H_2O$$
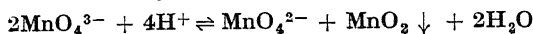
Mn(VI)

In this state Mn shows similarities to Cr, Mo, W and S. Mn(VI) is only found in solution as manganate ions, MnO_4^{2-}. These solutions are green, and the ions are only stable when the solution is very alkaline. They disproportionate in less alkaline solution:

$$3MnO_4^{2-} + 4H^+ \rightleftharpoons 2MnO_4^- + MnO_2 \downarrow + 2H_2O$$
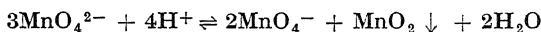
Mn(VII)

Mn is only found in this state in the permanganate ion MnO_4^-, reddish violet. This ion has similarities to ClO_4^-, IO_4^-, and ReO_4^-.

Mn_2O_7 is known in the form of explosive violet vapours which are obtained by dehydrating agents such as conc. H_2SO_4 on $HMnO_4$. Like $HClO_4$, $HMnO_4$ is a strong acid.

Redox

$$Mn^{2+} + 2e \rightleftharpoons Mn \downarrow \quad E_0 = -1.05 \text{ volts (calc.)}$$
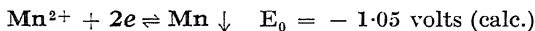
The metal is a strong reductant, and acts upon H_2O slowly.

$$Mn^{3+} + e \rightleftharpoons Mn^{2+} \quad E_0 = 1.51 \text{ volts (calc.)}$$

Formal potentials

In 25N-H_3PO_4	.	. .	1·27 volts
,, 9–15N-H_2SO_4	.	. .	1·49–1·50 volts
,, 0·3M-$H_4P_2O_7$	.	. .	1·23 volts at pH 0·8

$$Mn(H_2P_2O_7)_2^{2-}/Mn(H_2P_2O_7)_3^{3-} \quad E_0 = 1.15 \text{ volts}$$

$$Mn(IV) + 2e \rightleftharpoons Mn(III)$$

Formal potentials

In 25N-H_3PO_4	. . . . . .	1·47 volts
,, 9N-H_2SO_4	. . . . . .	1·57 volts; in 15N 1·05 volts
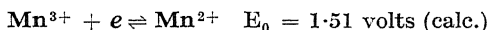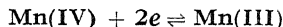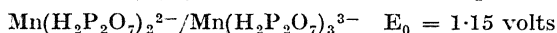
$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O \quad E_0 = 1.23 \text{ volts}$$
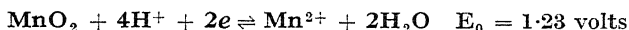
In 6N-HCl (complexes) the formal potential is 1·47 volts. MnO_2 oxidizes hot conc. HCl. Mn^{2+} can be oxidized to MnO_2 by conc. HNO_3. MnO_4^- oxidizes Mn^{2+} to MnO_2, more rapidly in the hot.

In alkaline solution.—$Mn(OH)_2$ oxidizes in the air as soon as it is precipitated, more rapidly in the presence of oxidants such as ClO^-, H_2O_2, $S_2O_8^{2-}$, etc. Mn_3O_4, Mn_2O_3, and MnO_2 are obtained in succession.

In 10N-NaOH, oxidation yields successively brown Mn_3O_4, then Mn_2O_3, and finally MnO_2 (probably as low-solubility Na_2MnO_3).

Formal potentials

MnO $\downarrow$ /$Mn_3O_4 \downarrow$	. . . . .	− 0·4 volt
$Mn_3O_4 \downarrow$ /$Mn_2O_3 \downarrow$	. . . . .	− 0·2 ,,
$Mn_2O_3 \downarrow$ /$MnO_2 \downarrow$	. . . . .	− 0·05 ,, at pH 14

The decomposition of H_2O_2 is catalysed by these redox systems.

$$MnO_4^{2-} + 4H^+ + 2e \rightleftharpoons MnO_2 \downarrow + 2H_2O$$
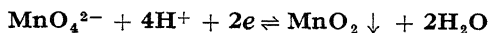
Formal potential is 0·6 volt in N-NaOH and 0·3 volt in 10N-NaOH. MnO_2 (or Na_2MnO_3) can thus be oxidized to manganates.

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-} \qquad E_0 = 0·54 \text{ volt}$$

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 \downarrow + 2H_2O \qquad E_0 = 1·67 \text{ volts}$$
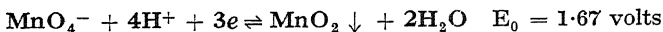
The reaction is very slow from left to right.

Formal potential is 1·50 volts in N-HClO$_4$. The permanganates are very strong oxidants. The potential falls when the pH increases (fig. 48) but it still remains very high. In acids, MnO_4^- oxidizes rapidly. It is reduced in general right down to Mn^{2+}, because the potentials of the systems $Mn(VII)/Mn(IV)$ and $Mn(IV)/Mn(II)$ are then very near to one another (fig 48). However, Mn^{2+} reacts slowly to give $Mn(IV)$. In acid solution,
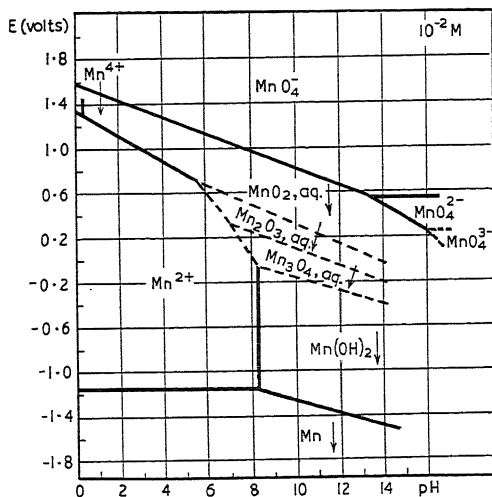
FIG. 48.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF MANGANESE AS A FUNCTION OF pH

MnO_4^- causes ferrous o-phenanthroline to change from red to pale blue, (1·1 volts). It oxidizes Fe^{2+}, conc. HCl, Cl^- in the hot, Sn^{2+}, $C_2O_4^{2-}$ in the hot, H_2O_2, S^{2-}, As(III), N_3^-, etc. In acetate buffer, Br^- and I^- are oxidized but not Cl^-.

In solution of low acidity, neutral or alkaline, only powerful reductants reduce permanganates right down to Mn^{2+}; generally the reaction stops at MnO_2. However, in the presence of ions which complex Mn^{3+}, for example F^-, the reduction can go to the $Mn(III)$ stage. Inversely, Mn^{2+} is only oxidized slowly in acids. Mn^{2+} is oxidized to MnO_4^- by $NaBiO_3$ in the cold, IO_4^- in the hot, Ag^{2+} in the cold or by $S_2O_8^{2-}$ + Ag^+ in the hot, and by PbO_2 in the presence of hot nitric acid.

At about pH 12–13 the $MnO_4^-/MnO_2 \downarrow$ system is replaced by the systems MnO_4^-/MnO_4^{2-} and $MnO_4^{2-}/MnO_2 \downarrow$. Thus the reduction of MnO_4^- goes through the stage of manganates.

$$Mn(CN)_6^{4-} - e \rightleftharpoons Mn(CN)_6^{2-} \qquad E_0 = -0·22 \text{ volt}$$
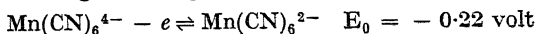
Disproportionations.—It can be seen from fig. 48 that Mn_2O_3,aq. disproportionates into MnO_2 and Mn^{2+} in acids.

$$Mn_2O_3 \downarrow + 2H^+ \rightleftharpoons MnO_2 \downarrow + Mn^{2+} + H_2O$$
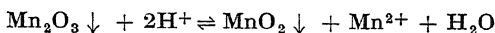
Mn^{3+} does not exist on account of the very low solubility of MnO_2.

$MnO_4{}^{2-}$ does not exist below pH 13·5; in less alkaline solution, we have

$$3MnO_4{}^{2-} + 4H^+ \rightleftharpoons 2MnO_4{}^- + MnO_2 \downarrow + 2H_2O$$
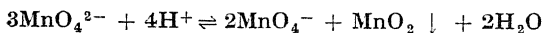
Similarly $MnO_4{}^{3-}$ can only exist in excessively alkaline solution.

Detection

Formation of permanganate ion.—(*a*) **By persulphate.**—Manganous salts in solution are oxidized by persulphate in the presence of Ag salts.

Solutions and materials required.—Sodium or potassium persulphate. 25 per cent silver nitrate.

Procedure.—To 1 drop of the solution to be examined add enough silver nitrate to precipitate all the chloride present—2 drops suffice; then 1 drop of conc. HNO_3 and a crystal of persulphate. Warm. A violet coloration appears if Mn(II) was present initially.

Concentration limit.—5.10^{-5} g.-ion of Mn^{2+} per litre (3 p.p.m.). This limit is so low that care must be taken not to mistake traces for considerable quantities. This can be done by diluting the solution before test.

Interfering substances.—The reaction is specific.

If much Cl^- is present, large quantities of silver nitrate have to be added in order to precipitate it completely. It is better therefore to remove it initially as HCl by adding H_2SO_4 and heating.

If the Mn^{2+} concentration is too high ($\geqslant$ 0·01M) the $MnO_4{}^-$ formed can be reduced by the Mn^{2+} remaining, and brown MnO_2 will be thrown down. In this case, also, the remedy is to dilute the solution.

If the excess of persulphate or of $AgNO_3$ is too large, black AgO will be formed slowly.

If there is much H_3PO_4, a violet-red complex with Mn(III) or Mn(IV) will be formed.

Cr^{3+} gives yellow to orange $Cr_2O_7{}^{2-}$. Ce(III) gives Ce(IV) (yellow to orange). V(IV) gives V(V) having the same colour. The sensitivity is slightly reduced. Fe(III) in nitric acid only gives a very weak coloration.

Among the coloured ions, Co^{2+} is the most troublesome. If its concentration is as high as 0·1 g.-ion/litre, the concentration limit is reduced to around 10^{-3} g.-ion/litre, even when using a cobalt solution of the same concentration as a comparison standard.

(*b*) **By periodate.**—Manganous salts are oxidized by periodates in hot acid solution.

Material required.—Solid potassium periodate.

Procedure.—To 1 drop of solution, add a few small crystals of solid periodate, and 1 drop of concentrated nitric acid. Boil. A red coloration appears and remains stable, if Mn(II) is present.

Concentration limit.—5.10^{-4} g.-ion of Mn^{2+} per litre (30 p.p.m.).

Interfering ions.—The reaction is specific. Cl^- does not interfere. The reaction is easier and the coloration more stable than with the persulphate, but it is less sensitive.

(*c*) **By bismuthate.**—Manganese salts are oxidized by sodium bismuthate in cold acid solution.

Material.—Solid sodium bismuthate.

Procedure.—The diluted solution is acidified with H_2SO_4 (dil.); shake for a few seconds with a little bismuthate. If very pale colours have to be observed, the solution must be filtered through an asbestos pad.

Interfering ions.—The reaction is specific.

Concentration limit.—5.10^{-4} g.-ions of Mn^{2+} per litre (30 p.p.m.).

RHENIUM

Re = 186·3

This element shows similarities to manganese and also to molybdenum. It can exist in every state of oxidation from I to VII. The important states are IV and VII in which the element behaves like manganese.

VI*a*	VII*a*
	Mn
Mo	Tc
W	Re

Re(IV).—The main representative is ReO_2,aq., black, analogue of MnO_2,aq. Soluble in conc. HCl with formation of complexes.

Re(V)

In acids gives green solutions. Disproportionates slowly in acids to Re(VII) and Re(IV). Oxalate complexes, and also more stable tartrate ones. These are blue to green.

Re(VI).—Represented by the ion ReO_4^{2-} in alkaline solution. Disproportionates.

Re(VII)

Represented by the strong acid $HReO_4$. ReO_4^- is colourless. The solubility of $KReO_4$ is fairly low (0·95 g./litre). The Ag^+, Tl^+, Cs^+, and Rb^+ salts are of fairly low solubility. Low-solubility salts with organic bases, in particular the salt Ph_4AsReO_4, which is soluble in chloroform.

Redox

$$ReO_4^- + 4H^+ + 3e \rightleftharpoons ReO_2 \downarrow + 2H_2O \quad . \quad . \quad \sim 0\cdot3 \text{ volt}$$

$$ReO_4^- + 8H^+ + 6Cl^- + 3e \rightleftharpoons ReCl_6^{2-} + 4H_2O \quad . \quad . \quad \sim 0\cdot5 \text{ ,, in}$$
$$6\text{–}10\text{N-HCl}$$
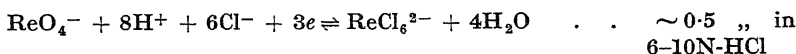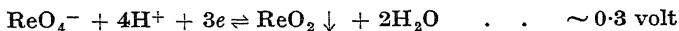
The system Re(VII)-Re(V) has remarkable catalytic properties. ReO_4^- is easily reduced by stannous chloride. Metallic Re is easily attacked by oxidants.

Detection of Re.—The problem is the detection of traces. It is thus really a problem of quantitative analysis.

Detection with thiocyanate.—The reaction is entirely similar to that with molybdenum (p. 240). When it is desired to detect traces of rhenium

in the presence of much Mo, which is what usually happens, the best method is to extract the Re(VII) in the form of tetraphenylarsonium perrhenate with chloroform.

NICKEL

$$Ni = 58.7$$

Very similar to cobalt, from which it differs in the main by the lesser importance of its oxidation state (III).

States of oxidation.—The element can exist in every state from I to IV. In aqueous solution, only II is known, in which the element is similar to Fe(II), Zn(II), Mn(II), Co(II), Cu(II); III and IV are known in solid compounds.

Ni(II).—Influence of pH.—The cation Ni^{2+} is green. In principle the pale green hydroxide $Ni(OH)_2$ precipitates above pH 7·2, but in practice basic salts or pale green adsorption compounds are formed instead.
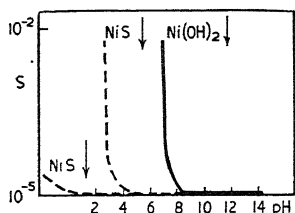
FIG. 49.—APPARENT SOLUBILITY OF Ni(II) SULPHIDE AND HYDROXIDE AS A FUNCTION OF pH

Complexes.—Very unstable chloride and sulphate complexes. Blue ammine complexes, rather unstable (analogues of the cupriammine complexes); oxalate, thiocyanate, metaphosphate and pyrophosphate ones are known; those formed with the anions of hydroxylated organic compounds are in general green and fairly unstable. The cyanide complexes are stable.

Low-solubility compounds.—There are many. The ferri- and ferrocyanides are the least soluble, along with the sulphide NiS and the dimethylglyoxime complex (red). NiS precipitates at pH 3·4–4·8, i.e. in acetate buffer at pH 4·5 (difference from MnS). The precipitated sulphide ages rapidly and its solubility in N-HCl becomes very low. The variation of solubility can be explained partly by a change in the dimensions of the particles of precipitate, and partly by a conversion of the sulphide to other modifications. In $(NH_4)_2S$, NiS can remain in colloidal solution; such solutions have a very deep colour. It dissolves slightly in sodium sulphide.

Equilibrium constants

$$Ni(OH)_2 \downarrow \rightleftharpoons Ni^{2+} + 2OH^- \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 15·2; \ 17·2; \ 18·1$$
$$Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+ \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 9·3$$
$$NiCO_3 \downarrow \rightleftharpoons Ni^{2+} + CO_3^{2-} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 6·9$$
$$NiC_2O_4 \downarrow \rightleftharpoons Ni^{2+} + C_2O_4^{2-} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 7·0$$
$$Ni(C_2O_4)_2{}^{2-} \rightleftharpoons Ni^{2+} + 2C_2O_4^{2-} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 6·5$$
$$Ni(CN)_4{}^{2-} \rightleftharpoons Ni^{2+} + 4CN^- \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 15·3; \ 22$$
$$Ni[Ni(CN)_4] \downarrow \rightleftharpoons Ni^{2+} + Ni(CN)_4{}^{2-} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 8·7$$
$$Ni(NH_3)_6{}^{2+} \rightleftharpoons Ni(NH_3)_5{}^{2+} + NH_3; \quad pk_6 = -0·09; \quad pk_5 = 0·6;$$
$$pk_4 = 1·1; \quad pk_3 = 1·6; \quad pk_2 = 2·1; \quad pk_1 = 2·7$$
$$Ni(N_2H_4)^{2+} \rightleftharpoons Ni^{2+} + N_2H_4 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 1$$
$$NiS \downarrow \rightleftharpoons Ni^{2+} + S^{2-} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad 20·5–27·7$$

Ni(III).—The cation does not exist but only Ni_2O_3 over the whole pH range; this is not stable and reacts slowly with water, releasing oxygen.

No complexes are known (apart from nickelic dimethylglyoxime) (difference from cobalt).

Ni(IV)

NiO_2 black, not stable, reacts rapidly with water with liberation of oxygen.

Redox.—(1) $\quad Ni \downarrow \; - 2e \rightleftharpoons Ni^{2+} \quad E_0 = -0.24$ volt

slow in both directions.

$$Ni \downarrow \; + 2H^+ \rightleftharpoons Ni^{2+} + H_2$$
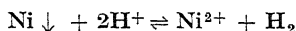
The over-potential of hydrogen on nickel is 0·20 volt. Nickel is little attacked by HCl and H_2SO_4. Oxidizing acids dissolve it: HNO_3 or hot conc. H_2SO_4.

(2) In alkaline solution, the following formal potentials are set up:

$3NiO \downarrow \; + H_2O - 2e \rightleftharpoons Ni_3O_4 \downarrow \; + 2H^+ \quad . \quad . \quad . \quad . \quad \sim 0.0$ volt
$2Ni_3O_4 \downarrow \; + H_2O - 2e \rightleftharpoons 3Ni_2O_3 \downarrow \; + 2H^+ \quad . \quad . \quad . \quad \sim 0.5$,,
$Ni_2O_3 \downarrow \; + H_2O - 2e \rightleftharpoons 2NiO_2 \downarrow \; + 2H^+ \quad . \quad . \quad . \quad . \quad \sim 0.6$,,
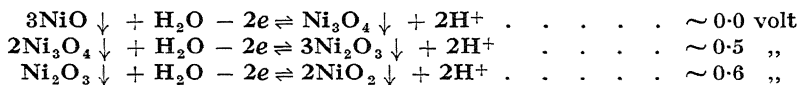
(solutions saturated with oxides).

NiO_2 reacts rapidly with water, hence it is practically non-existent:

$$\frac{2NiO_2 \downarrow \; + 2H^+ + 2e \longrightarrow Ni_2O_3 \downarrow \; + H_2O}{\qquad\qquad H_2O - 2e \longrightarrow 2H^+ + \tfrac{1}{2}O_2 \uparrow}$$
$$2NiO_2 \downarrow \; \longrightarrow Ni_2O_3 \downarrow \; + \tfrac{1}{2}O_2 \uparrow$$
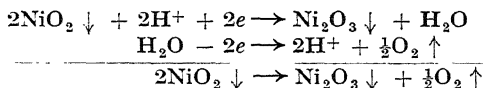
Ni_2O_3 itself also reacts with water, but more slowly:

$$\frac{3Ni_2O_3 \downarrow \; + 2H^+ + 2e \longrightarrow 2Ni_3O_4 \downarrow \; + H_2O}{\qquad\qquad H_2O - 2e \longrightarrow 2H^+ + \tfrac{1}{2}O_2 \uparrow}$$
$$3Ni_2O_3 \downarrow \; \longrightarrow 2Ni_3O_4 \downarrow \; + \tfrac{1}{2}O_2 \uparrow$$
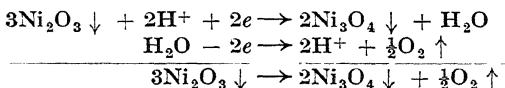
It can therefore be observed for some time.

In alkaline solution $Ni(OH)_2$ does not oxidize at any appreciable rate in air (difference from $Mn(OH)_2$, $Co(OH)_2$, $Fe(OH)_2$); but oxidants can produce from it in succession Ni_3O_4, Ni_2O_3, and NiO_2. As NiO_2 is not stable, it reacts with water and is reduced to a mixture of the other two oxides (Ni_3O_4 and Ni_2O_3). The oxidant oxidizes these oxides once again, and the oxidation of water by the oxidant thus brought about is catalysed rapidly by the system NiO_2/Ni_2O_3, and slowly by the system Ni_2O_3/Ni_3O_4. Thus hypochlorites oxidize water:

$$\frac{ClO^- + 2H^+ + 2e \longrightarrow Cl^- + H_2O}{\qquad\qquad H_2O - 2e \longrightarrow 2H^+ + \tfrac{1}{2}O_2 \uparrow}$$
$$ClO^- \longrightarrow Cl^- + \tfrac{1}{2}O_2 \uparrow$$
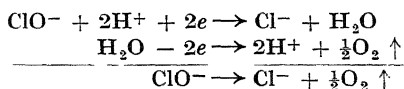
In the presence of nickel oxide, hypochlorites are not stable. The same is true for all the oxidants which oxidize CoO to CoO_2.

The decomposition of H_2O_2 is also catalysed.

IO_3^-, O_3, H_2O_2 all give only Ni_3O_4; ClO^-, $S_2O_8^{2-}$, BrO^- in excess give Ni_2O_3; MnO_4^-, IO_4^- give a mixture of the two hydrated oxides.

14

Fig. 50 shows that in acid solution neither Ni_3O_4 nor Ni_2O_3 exist, they disproportionate into NiO_2 and Ni^{2+} and, as NiO_2 is not stable in aqueous solution, we get finally Ni^{2+} and oxygen gas.

$$Ni(CN)_4{}^{2-}/Ni(CN)_3{}^{2-} \quad . \ . \ . \ . \ . \ . \ - 0\cdot6 \text{ volt}$$
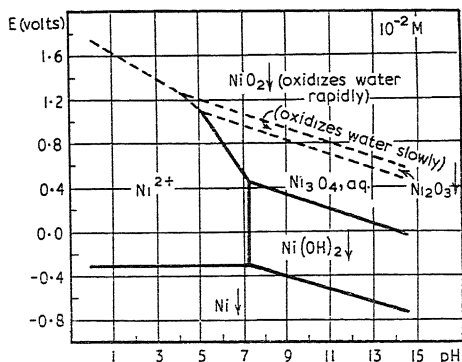
FIG. 50.—NORMAL FORMAL POTENTIALS OF THE REDOX SYSTEMS OF NICKEL AS A FUNCTION OF pH

Detection

Dimethylglyoxime.—Dimethylglyoxime gives with salts of nickel, in acid, neutral, or ammoniacal solution, a red precipitate of nickel dimethylglyoxime.

$$CH_3—C{=}NOH \quad HON{=}C—CH_3$$
$$CH_3—C{=}NO—Ni—ON{=}C—CH_3$$
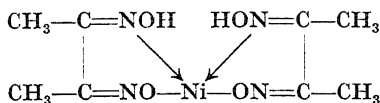
Solutions and materials required.—1 per cent alcoholic solution of dimethyl-glyoxime. Solid sodium acetate.

Procedure.—To 1 drop of solution, add several crystals of sodium acetate followed by 2 drops of the dimethylglyoxime solution. When the solution to be examined is dilute, use larger quantities.

Concentration limit.—$5 . 10^{-5}$ g.-ion of Ni^{2+} per litre (3 p.p.m.).

Interfering substances.—(1) In sufficiently strong acid, the complex is destroyed with liberation of free DMG; in strongly alkaline solution $Ni(OH)_2$ is formed. Hence the test is carried out in acetate buffer, by adding solid acetate to the acid.

(2) Powerful oxidants and reductants must be counteracted by the addition of an excess of reagent.

(3) Fe^{2+}, in the presence of a mixture of NH_3 and $NH_4{}^+$, gives a red complex (p. 166) which can be oxidized by a crystal of per-sulphate.

With Cu^{2+}, Mn^{2+}, Fe^{3+} the same inconveniences are met with as in the detection of Fe^{2+} (see p. 166). Proceed thus: complex the Fe^{3+} with an excess of solid fluoride. Cu^{2+} and Mn^{2+} give interfering brown colours, whose appearance is avoided by adding, for Cu^{2+}, 1 or 2 drops

of bisulphite, then 1 drop of thiocyanate, and for Mn^{2+}, 1 or 2 drops of bisulphite alone. Then introduce the reagents.

When Co^{2+} and Zn^{2+}, which use up the reagent, are present, an excess of the latter must be used.

In the presence of much Co^{2+} the reaction cannot be used to detect nickel. In this case, the following separation can be carried out, permitting the detection of 1 part of nickel in the presence of 100 parts of Co: the peroxides of both Ni and Co are first precipitated, then the solution is made ammoniacal in the presence of dimethylglyoxime; only Ni goes into solution, giving a bright red coloration of nickelic dimethylglyoxime.

Materials required.—4N-NaOH. Conc. NH_3. Solid $K_2S_2O_8$.

Procedure.—Place 3 drops of solution in a centrifuge tube along with some crystals of persulphate. Boil. The black oxides of Ni and Co precipitate. Centrifuge. Decant the liquid. Redissolve with 3–4 drops of dimethylglyoxime and a drop of ammonia. Shake vigorously. Centrifuge in order to distinguish the coloration due to nickel.

COBALT

Co = 58·9

States of oxidation.—II in which Co resembles Fe(II), Ni(II), Zn(II), Cu(II); III is represented almost entirely by complexes; IV-CoO_2, analogue of NiO_2 and MnO_2.

Co(II)

Influence of pH.—The cation Co^{2+} is pink. The pink hydroxide precipitates in theory at pH 7·5 (0·01M); but in practice basic salts or adsorption compounds which are pink or blue come down. $Co(OH)_2$ redissolves very slightly in very strong alkali. It oxidizes in the air, going brown.

Complexes.—$Co(OH)_2$ dissolves in a mixture of $NH_3 + NH_4^+$ by formation of ammines which oxidize rapidly in the air giving red cobaltiammines (Co(III)).

Low-stability chloride complexes are formed, which in concentrated Cl^- are blue. With CNS^- the same colorations are obtained, first magenta, then blue. Complexes of rather low stability are given with hydroxylated organic compounds:

FIG. 51.—APPARENT SOLU-
BILITY OF Co(III) AND
Co(II) HYDROXIDES AS A
FUNCTION OF pH

with glycerol, a yellow coloration is obtained. Cyanide complexes are obtained which are fairly stable, but which oxidize in the air.

Low-solubility compounds.—These are numerous: pink and blue. The ferro- and ferricyanides are the least soluble. Black CoS precipitates at pH 4·5–4·8. Like NiS, it ages rapidly and its solubility in N-HCl becomes small.

Organic solvents.—A certain number of complexes, such as $H_2Co(CNS)_4$, give blue solutions in various organic solvents. The addition of a liquid miscible with water such as alcohol, acetone, etc., decreases the ionization and thus permits the blue coloration to appear: $CoCl_4^{2-}$, $CoCl_3^-$, $CoCl_2$.

Equilibrium constants

$$Co(OH)_2 \downarrow \rightleftharpoons Co^{2+} + 2OH^- \quad . \quad . \quad . \quad . \quad 14 \cdot 9 – 17 \cdot 8$$
$$Co(OH)_2 \downarrow \rightleftharpoons HCoO_2^- + H^+ \quad . \quad . \quad . \quad . \quad 19 \cdot 1$$
$$CO(NH_3)_6{}^{2+} \rightleftharpoons Co(NH_3)_5{}^{2+} + NH_3; \quad pk_6 = -0 \cdot 6; \quad pk_5 = -0 \cdot 2;$$
$$pk_4 = 0 \cdot 8; \; pk_3 = 1 \cdot 0; \; pk_2 = 1 \cdot 6; \; pk_1 = 2 \cdot 1 \text{ for } I = 2$$
$$CoC_2O_4 \downarrow \rightleftharpoons Co^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 5 \cdot 4$$
$$CoCO_3 \downarrow \rightleftharpoons Co^{2+} + CO_3{}^{2-} \quad . \quad . \quad . \quad . \quad 12 \cdot 0$$
$$Co(CN)_6{}^{4-} \rightleftharpoons Co^{2+} + 6CN^- \quad . \quad . \quad . \quad . \quad 19 \cdot 1$$
$$Co(CN)_2 \downarrow \rightleftharpoons Co^{2+} + 2CN^- \quad . \quad . \quad . \quad . \quad 7 \cdot 8$$
$$CoS \downarrow \rightleftharpoons Co^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad . \quad 22 \cdot 2 – 26 \cdot 7$$
$$Co(\alpha\text{-nitroso–}\beta\text{-naphthol})_2 \downarrow \; \rightleftharpoons Co^{2+} + 2(\alpha\text{-nitroso–}\beta\text{-naphthol})^- \quad 16 \cdot 3$$
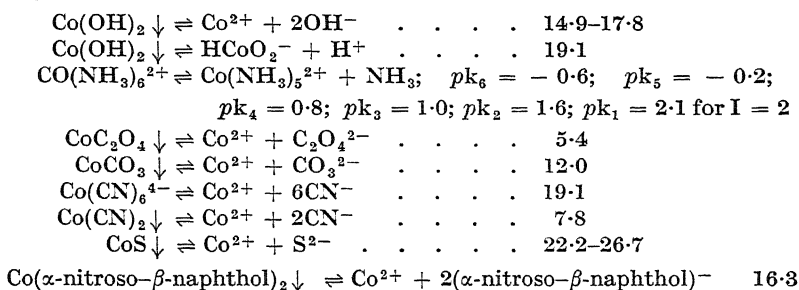
Co(III)

The cation Co^{3+} exists in very acid solution. Co_2O_3,aq., brownish-black, precipitates at around $pH\ 0 \cdot 5\ (0 \cdot 01M)$.

Co(III) exists mainly in the form of complexes, which are yellow or red. Some of them are extremely stable, such as $Co(CN)_6{}^{3-}$; the cobalti-ammines, which are strong bases, are sometimes stable in strong acids and alkalis. Fairly stable oxalate and nitrite complexes are known.

Equilibrium constants

$$Co(OH)_3 \downarrow \rightleftharpoons Co^{3+} + 3OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 42 \cdot 6$$
$$Co(NH_3)_6{}^{3+} \rightleftharpoons Co(NH_3)_5{}^{3+} + NH_3; \quad pk_6 = 4 \cdot 4; \quad pk_5 = 5;$$
$$pk_4 = 5 \cdot 6; \quad pk_3 = 6 \cdot 1; \quad pk_2 = 6 \cdot 7;$$
$$pk_1 = 7 \cdot 3 \ (I = 2)$$

Redox

(1) $\qquad Co \downarrow - 2e \rightleftharpoons Co^{2+} \quad E_0 = -0 \cdot 28$ volt (slow)
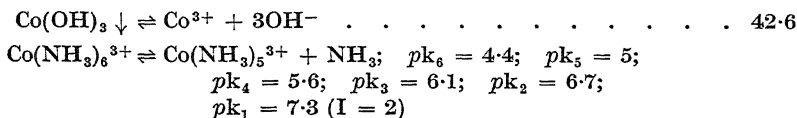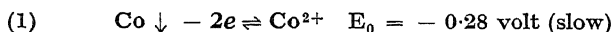
Cobalt in acid solution is a little stronger reductant than nickel; it is more easily attacked by dilute acids.

In KOH saturated with oxide, we have

$$Co \downarrow + 2OH^- - 2e \rightleftharpoons Co(OH)_2 \quad E'_0 = -0 \cdot 73 \text{ volt}$$

In $6N\text{-}NH_3$ we have

$$Co \downarrow + 6NH_3 - 2e \rightleftharpoons Co(NH_3)_6{}^{2+} \quad E'_0 = -0 \cdot 56 \text{ volt}$$
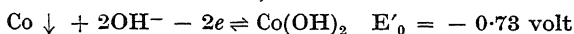
(2) In alkaline solution, we have the following systems, with their formal potentials in 7N-KOH.

$$3CoO \downarrow + H_2O - 2e \rightleftharpoons Co_3O_4 \downarrow + 2H^+ \quad . \quad . \quad . \quad . \quad +0 \cdot 01 \text{ volt}$$
$$2Co_3O_4 \downarrow + H_2O - 2e \rightleftharpoons 3Co_2O_3 \downarrow + 2H^+ . \quad . \quad . \quad . \quad +0 \cdot 11 \quad ,,$$
$$Co_2O_3 \downarrow + H_2O - 2e \rightleftharpoons 2CoO_2 \downarrow + 2H^+ \quad . \quad . \quad . \quad +0 \cdot 65 \quad ,,$$
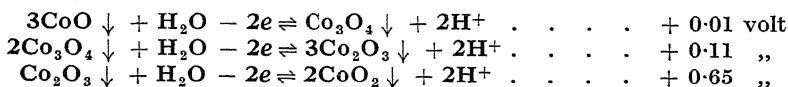
(solutions saturated with oxides).

If we compare these with the properties of nickel oxides, we shall see that the potentials of the two sets of systems are not much different from

one another. Only the Co_3O_4/Co_2O_3 system has a potential lower (by 0·4 volt) than that of the Ni_3O_4/Ni_2O_3 system. As a result, Co_2O_3 is a much poorer oxidant than Ni_2O_3; its region of existence is much larger; it does not react with water and exists even in very acid solution as Co^{3+}.

The III oxidation state of cobalt is much more important than the corresponding state of nickel.

CoO_2, like NiO_2, reacts with water quite rapidly. The system CoO_2/Co_2O_3 will thus catalyse the oxidation of water by ClO^-, etc., and hypochlorite ions are therefore not stable in aqueous solutions containing cobalt salts. The decomposition of hydrogen peroxide is also catalysed (see p. 276).
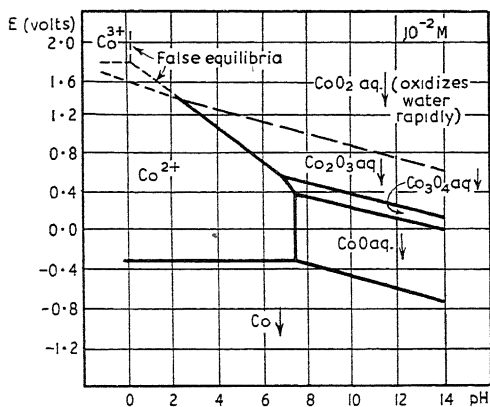
FIG. 52.—APPROXIMATE VALUES OF FORMAL NORMAL POTENTIALS
OF THE REDOX SYSTEMS OF COBALT AS A FUNCTION OF pH

In alkaline solution, $Co(OH)_2$ oxidizes rapidly in the air, giving Co_3O_4, more rapidly in the presence of oxidants.

Thus hydrogen peroxide yields $Co_2O_3 + Co_3O_4$ and ClO^-, BrO^-, IO^-, $S_2O_8^{2-}$ and MnO_4^- give $Co_2O_3 + CoO_2$. IO_4^- gives Co_2O_3.

In acid solution we have

$$Co^{2+} - e \rightleftharpoons Co^{3+} \quad E_0 = 1·84 \text{ volts}$$
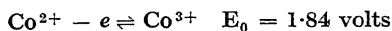
The salts of Co(III) are not stable. They disproportionate slowly into Co^{2+} and CoO_2, the latter reacts rapidly with water, and the final result is Co^{2+} and oxygen gas.

Inversely, it is difficult to oxidize Co^{2+} to Co^{3+}, except by electrolysis and the formation of complexes.

$$(3) \quad Co(CN)_6^{3-} + e \rightleftharpoons Co(CN)_6^{4-} \quad E_0 = -0·83 \text{ volt}$$
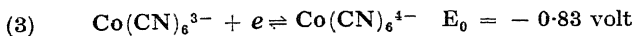
The system is a strong reductant; cobaltocyanides oxidize rapidly in the air.

Detection

(1) **Thiocyanate.**—Co^{2+} ions give complex blue ions with thiocyanates, not much ionized in the presence of various organic solvents which dissolve them: alcohol, acetone, aniline, benzyl alcohol, etc.

Solutions and materials required.—Saturated solution of NH_4CNS.
    Benzyl alcohol.
    M-$NaHSO_3$.
    Solid NaF.

Procedure.—Use a test plate. To 1 drop of solution, add 1 drop of thio-cyanate. The coloration due to Fe^{3+} appears if the latter is present; that which is due to Co^{2+} is not sensitive. Add then a little NaF to make the red coloration disappear. Add 1 drop of benzyl alcohol: shake. The blue colour due to the cobalt appears in the alcohol.

Concentration limit.—2.10^{-2} g.-ion of Co^{2+} per litre (1000 p.p.m.) in the absence of solvent; 3.10^{-4} in the presence of benzyl alcohol ($= 20$ p.p.m.).

Interfering substances.—(1) CNS^- is not basic; $Co(OH)_2$ precipitates in alkaline solution. The test must therefore be made in acid or neutral solution.

    (2) Oxidants which oxidize CNS^- must be counteracted with an excess of reagent.

    (3) Ions which complex CNS^-, like Hg^{2+}, must be counteracted by an excess of reagent.

    Ferric ions give a red coloration which can be made to disappear by complexing the Fe^{3+} with F^-. Cu^{2+} gives a brown coloration of $Cu(CNS)_2$ which can be removed with 1 drop of bisulphite. Ti(IV) gives an orange coloration, which disappears when F^- is added. Bi(III), UO_2^{2+}, Mo(VI), etc., give yellow or orange colorations which do not interfere much. Ni^{2+} gives a green coloration in strong concentration. VO_2^+ gives a blue coloration, insoluble in ether. VO^{2+} gives a violet coloration, also insoluble in ether.

    The coloration due to Co^{2+} is soluble in ether, like those of Ti(IV), Mo(VI) and to some extent that of Cu^{2+}.

    The precious metals give colorations which can interfere.

    Co^{2+} is detected at the same time as Fe^{3+} (see p. 165).

    (2) **Mercurithiocyanate** (see p. 187).—In acid or neutral solution, ammonium mercurithiocyanate gives a deep blue crystalline precipitate of cobalt mercurithiocyanate. The crystals form at the surface of the solution, then fall to the bottom of the test-tube. In the presence of a small quantity of a zinc salt, mixed crystals of the mercurithiocyanates of zinc and cobalt are formed immediately, the blue colour of which is paler in proportion as the amount of zinc salt is higher.

Solution required.—Solution of ammonium mercurithiocyanate.

Mercuric chloride	30 g
Ammonium thiocyanate	33 g
Water	100 ml
1 per cent $ZnCl_2$	

Procedure.—Use a test plate. To 1 drop of solution add 2 drops of reagent. Wait.

    A white precipitate indicates Zn alone, 10^{-3} (60 p.p.m.).
    A deep blue precipitate indicates Co alone, 5.10^{-3} (300 p.p.m.).
    A mauve to black precipitate indicates Zn + Cu.

A sky-blue precipitate indicates Zn + Co.

It is more sensitive to detect Co^{2+} after the addition of 1 drop of the zinc solution at 10^{-4} g.-ion/litre (6 p.p.m.).

Procedure.—To 1 drop of solution, add 1 or 2 drops of reagent. Rub the sides of the test-tube with a stirring rod.

Concentration limit.—5.10^{-3} g.-ion of Co^{2+} per litre (300 p.p.m.). The presence of zinc sensitizes the reaction. Mix in beforehand 1 drop of zinc salt solution with 1 drop of the test solution. The limit is then 10^{-4} g.-ion of Co^{2+} per litre, or 6 p.p.m.

Interfering substances.—(1) In very acid solution, the complex is destroyed by the formation of HCNS; in alkalis, HgO (yellow) precipitates.

(2) Sufficiently powerful reductants, Sn^{2+} for example, precipitate black Hg. An excess of reagent must be added for oxidants which oxidize CNS^-.

(3) An excess of reagent must be added when ions which form complexes with CNS^- are present. Some give coloured complexes (Fe^{3+}); these can be complexed beforehand by the addition of a little fluoride. VO^{2+} gives a blue coloration which is not carried down by the precipitate.

(4) Cu^{2+}, in the presence of Zn^{2+}, gives a violet or black precipitate which can mask the blue precipitate.

ZINC

Zn = 65·4

This element is found above cadmium in the periodic table. It is very similar to Cd, but Zn^{2+} is more acid than Cd^{2+} and gives anions.

Oxidation number.—II.

Influence of pH.—The Zn^{2+} cation is colourless, $Zn(OH)_2$ is white, and precipitates from pH 6·8 (0·01M). In general, neutralization involves the precipitation of basic salts or adsorption compounds which are converted to the hydroxide in more alkaline solution. $Zn(OH)_2$ is amphoteric, and redissolves above pH 13 giving $HZnO_2^-$ and then ZnO_2^{2-}, which are colourless. NH_3 dissolves the hydroxide with formation of ammine complexes.

Complexes.—The ammine, cyanide, thiocyanate complexes are fairly unstable; the oxalate ones are not stable. Chloride complexes such as $ZnCl_2$, $ZnCl^+$ are also not very stable.

FIG. 53.—APPARENT SOLUBILITY OF ZINC HYDROXIDE AS A FUNCTION OF pH

Low-solubility compounds.—There are many. ZnS is the least soluble: it is white, and colloidal when precipitated in alkaline solution. It can be flocculated with NH_4^+. It is easy to filter if it is precipitated in hot acid solution. (The particles are larger because the solubility is then larger.) It precipitates at a pH as low as 1·1 and thus comes down in chloroacetate buffer at pH 2·5 (difference from Mn^{2+}, Ni^{2+}, Co^{2+}).

Freshly precipitated, it redissolves in strong alkali. $K_2Zn_3(Fe(CN)_6)_2$ is white, and its solubility is low in very weak acid. Zinc cobalticyanide has the same properties. $ZnNH_4PO_4$, the analogue of ammonium–magnesium phosphate, is of low solubility between pH 5·5 and 7·5.

Equilibrium constants

$$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+ \quad . \quad . \quad . \quad . \quad . \quad 9·6\text{–}9·8$$
$$Zn(IO_3)_2 \downarrow \rightleftharpoons Zn^{2+} + 2IO_3^- \quad . \quad . \quad . \quad . \quad . \quad 5·4$$
$$ZnCO_3 \downarrow \rightleftharpoons Zn^{2+} + CO_3^{2-} \quad . \quad . \quad . \quad . \quad 7·0\text{–}10·0$$
$$Zn(C_2O_4)_3^{4-} \rightleftharpoons Zn^{2+} + 3C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad 9$$
$$Zn(NH_3)_4^{2+} \rightleftharpoons Zn^{2+} + 4NH_3 \quad . \quad . \quad . \quad . \quad 9·0$$
$$Zn(OH)_2 \downarrow \rightleftharpoons Zn^{2+} + 2OH^- \quad . \quad . \quad . \quad . \quad 15·8\text{–}17·1$$
$$Zn(OH)_2 \downarrow \rightleftharpoons ZnO_2^{2-} + 2H^+ \quad . \quad . \quad . \quad . \quad 29$$
$$Zn(CN)_4^{2-} \rightleftharpoons Zn(CN)_3^- + CN^- \quad . \quad . \quad . \quad -1; 2·7$$
$$Zn(CNS)_3^- \rightleftharpoons Zn^{2+} + 3CNS^- \quad . \quad . \quad . \quad . \quad 17·9$$
$$ZnS \downarrow \rightleftharpoons Zn^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad . \quad 22·9\text{–}25·2$$
$$Zn_3K_2(Fe(CN)_6)_2 \downarrow \rightleftharpoons 3Zn^{2+} + 2K^+ + 2Fe(CN)_6^{4-} \quad . \quad 95$$
$$Zn \text{ oxine}_2 \downarrow \rightleftharpoons Zn^{2+} + 2 \text{ oxine}^- \quad . \quad . \quad . \quad . \quad 20·4$$
$$Zn(P_2O_7)_2^{6-} \rightleftharpoons Zn^{2+} + 2P_2O_7^{4-} \quad . \quad . \quad . \quad . \quad 6·5 \text{ at } 35° \text{ C.}$$

Redox.—$Zn \downarrow - 2e = Zn^{2+}$ $E_0 = -0·76$ volt

In alkaline solution:

$$Zn \downarrow + 2OH^- - 2e \rightleftharpoons ZnO_2^{2-} + 2H^+ \quad E_0 = -1·22 \text{ volts}$$

The metal is a strong reductant. It is attacked by both acid and alkali. It is not attacked between pH 7 and 13 (low-solubility oxide). It is used in acid solution, sometimes as the amalgam, in a large number of reductions where a powerful reducing action is required: preparation of Cr^{2+} and V^{2+}. It reduces As(III) to AsH_3 and, in alkaline solution, NO_3^- to NH_3.
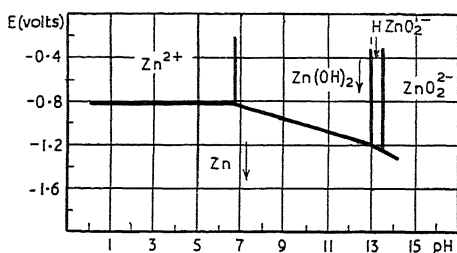
FIG. 54.—FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF ZINC AS A FUNCTION OF pH

Detection

Mercurithiocyanate. (See p. 187.)—Zinc salts give with mercurithiocyanate ion, $Hg(CNS)_4^{2-}$, a white precipitate of the zinc salt which is of low solubility in low-acidity solution. In the presence of Co^{2+} and Cu^{2+} the precipitation of cobalt and copper salts gives mixed crystals, and in the first case a blue, and in the second case a violet to black precipitate is obtained.

The reaction in the presence of Cu^{2+} is very sensitive and permits the detection of Zn^{2+}. However, Cd^{2+}, Ni^{2+}, Mn^{2+}, and Co^{2+}, in 0·1M to M solution can cause the same reaction. Hence the reaction is carried out and, if it is negative, the absence of Zn^{2+} is deduced. If it is positive, the test should be repeated after separating $Mn(OH)_2$, $Ni(OH)_2$, $Cd(OH)_2$, and $Co(OH)_2$ by 4N-NaOH in the hot; these precipitates can be centrifuged

out (see p. 86). Zn(II) can be detected at the same time as Co^{2+} and Cu^{2+} (see p. 200 and also p. 210.)

Solutions required.—Ammonium mercurithiocyanate:

Mercuric chloride	30 g
Ammonium thiocyanate	33 g
Water	100 ml

CuCl$_2$ solution: 0·5 per cent.

Procedure.—Use a test plate. Add 2 drops of reagent to 1 drop of solution. Wait.

A white precipitate indicates Zn^{2+} alone: 10^{-3} (60 p.p.m.).

A deep blue precipitate indicates Co^{2+} alone: 5.10^{-3} (300 p.p.m.).

A mauve to black precipitate indicates $Zn^{2+} + Cu^{2+}$.

A sky-blue precipitate indicates $Zn^{2+} + Co^{2+}$.

The sensitivity for Zn is increased by the prior addition of 1 drop of the CuCl$_2$ solution. It is then 5.10^{-4} g.-ion/litre, or 30 p.p.m.

Interfering substances.—If the concentration of Cu^{2+} is too high, the precipitate is coloured green by copper mercurithiocyanate. Repeat the test after diluting. If there is really too much copper, separate it with a little metallic aluminium; decant the supernatant liquid, reoxidize the solution with persulphate, destroy the excess of persulphate by boiling for 30 seconds.

If the concentration of Co(II) is too high, the formation of a deep blue ppt. of cobalt mercurithiocyanate can interfere. Repeat the test after dilution. If there is really too much Co^{2+}, convert it to a cobaltiammine by adding 1 drop of 5 vol. H$_2$O$_2$, and then 1 drop of ammonia (1/1). Reacidify with 2 drops of 4N-HCl, and carry out the test immediately.

Fe^{3+}, which gives a red colour with CNS$^-$, interferes. It also gives a violet colour to the precipitate. It must be complexed with F$^-$ by adding solid NaF. But, if Fe^{2+} is also present, it will, in the presence of F$^-$, become an energetic reductant and may reduce even Cu^{2+}. It must be oxidized with a little persulphate, the excess of this being destroyed as usual by boiling.

CADMIUM

$$Cd = 112\cdot4$$

In the periodic table, this appears below zinc, which it closely resembles. It is also analogous to copper in the II state of oxidation.

State of oxidation.—II

Ib	IIb	IIIb
Cu(I)	Zn(II)	In(III)
Ag(I)	Cd(II)	
	Hg(II)	

Influence of pH.—The cation Cd^{2+} is colourless, white Cd(OH)$_2$ precipitates from pH 8·3 (0·01M). In the hot, the precipitate yellows by dehydration. CdO is a deep brown. Cd(OH)$_2$ redissolves slightly in strongly alkaline solution: Cd(OH)$_4^{2-}$, Cd(OH)$_5^{3-}$, etc.

Neutralization yields at first basic salts and

adsorption compounds; thus the 'basic sulphate' exists up to a pH of 10·6, and is not completely converted to hydroxide until a pH of 11·2 is reached.

Low-solubility compounds.—A large number of salts and basic salts have a low solubility (carbonates, cyanides, phosphates, etc.). The sulphide is the least soluble. It is lemon-yellow to orange and is frequently
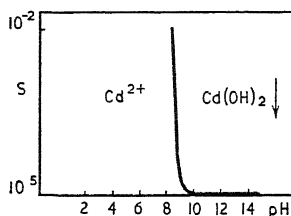
FIG. 55.—APPARENT SOLUBILITY OF CADMIUM HYDROXIDE
AS A FUNCTION OF pH

colloidal; it is insoluble even at pH 0·2. It is soluble in hot $7N\text{-}H_2SO_4$ (difference from copper). Its solubility in N-trichloroacetic acid is low in the cold (distinction from zinc). It is precipitated in $0\cdot3N\text{-}HCl$ and redissolves in more concentrated HCl. In HCl also, a precipitate of the chlorosulphide $(CdCl)_2S$ can be formed.

Complexes.—Most anions form complexes with Cd^{2+}. $CdCl^+$, $CdCl_2$, $CdCl_3^-$, $CdCl_4^{2-}$, similar complexes with CNS^-, Br^- and I^- are formed (only up to CdI_3^-); $CdNO_3$, $CdSO_4$, $Cd(SO_4)_2^{2-}$, with $S_2O_3^{2-}$, etc. All are of low stability.

The hydroxide $Cd(OH)_2$ redissolves in NH_3 with formation of ammine complexes which are not very stable. Similarly, the cyanide complexes are not very stable either: $CdCN^+$, $Cd(CN)_2$ of low solubility, $Cd(CN)_3^-$, $Cd(CN)_4^{2-}$.

Equilibrium constants

$$Cd(OH)_2 \downarrow \rightleftharpoons Cd^{2+} + 2OH^- \qquad \ldots \qquad 13\cdot5$$
$$CdCO_3 \downarrow \rightleftharpoons Cd^{2+} + CO_3^{2-} \qquad \ldots \qquad 13\cdot6$$
$$CdC_2O_4 \downarrow \rightleftharpoons Cd^{2+} + C_2O_4^{2-} \qquad \ldots \qquad 7\cdot8$$
$$CdC_2O_4 \rightleftharpoons Cd^{2+} + C_2O_4^{2-} \qquad \ldots \qquad 3\cdot5$$
$$Cd(C_2O_4)_2^{2-} \rightleftharpoons CdC_2O_4 + C_2O_4^{2-} \qquad \ldots \qquad 1\cdot8$$
$$Cd(IO_3)_2 \downarrow \rightleftharpoons Cd^{2+} + 2IO_3^- \qquad \ldots \qquad 7\cdot65$$
$$CdS \downarrow \rightleftharpoons Cd^{2+} + S^{2-} \qquad \ldots \qquad 27\cdot2\text{--}28\cdot4$$
$$CdCl^+ \rightleftharpoons Cd^{2+} + Cl^- \qquad \ldots \qquad \sim 2$$
$$Cd(S_2O_3)_4^{6-} \rightleftharpoons Cd(S_2O_3)_3^{4-} + S_2O_3^{2-} \qquad \ldots \qquad \sim 1\cdot1$$
$$Cd(S_2O_3)_3^{4-} \rightleftharpoons Cd^{2+} + 3S_2O_3^{2-} \qquad \ldots \qquad 6\cdot3$$
$$Cd(CN)_4^{2-} \rightleftharpoons Cd(CN)_3^- + CN^-; \quad pk_4 = 3\cdot6; \quad pk_3 = 4\cdot6;$$
$$Cd(CN)_2 \downarrow; \quad pk_2 = 5\cdot1; \quad pk_1 = 5\cdot5$$
$$Cdcitr.^- \rightleftharpoons Cd^{2+} + citr.^{3-} \qquad \ldots \qquad 4\cdot3$$
$$Cd(NH_3)_6^{2+} \rightleftharpoons Cd(NH_3)_5^{2+} + NH_3; \quad pk_6 = -1\cdot7, -0\cdot7;$$
$$pk_5 = -0\cdot3, -0\cdot4; \quad pk_4 = 0\cdot8; \quad pk_3 = 1\cdot3;$$
$$pk_2 = 2\cdot0; \quad pk_1 = 2\cdot5$$

Redox

$$Cd \downarrow - 2e \rightleftharpoons Cd^{2+} \quad E_0 = -0.40 \text{ volt}$$
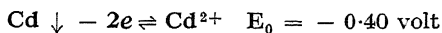
A much poorer reductant than zinc. It is mainly attacked by nitric and hot conc. sulphuric acids. Cadmium salts are reduced by zinc in neutral solution.

In 8N-KOH, $E'_0 = -0.8$ volt.
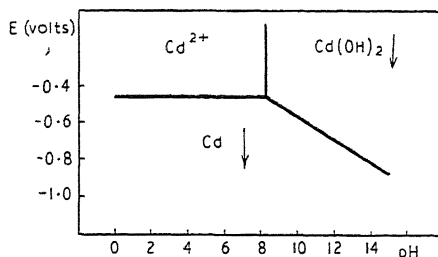
FIG. 56.—FORMAL NORMAL POTENTIALS OF THE
REDOX SYSTEMS OF CADMIUM

Detection.—As sulphide.—The formation of yellow cadmium sulphide is utilized (see p. 90).

Solutions required.—20 per cent KCN.

Saturated Na_2S.

Procedure.—To 2 drops of the sulphide solution, add 1 drop of the test solution. Wait.

Concentration limit.—10^{-4} g.-ion/litre of Cd^{2+} (100 p.p.m.).

Separation of interfering substances.—Numerous sulphides are coloured, and so the corresponding ions must be separated. A preliminary separation by NH_3 and NH_4^+ only leaves in solution the elements of the zinc group: Mn(II), Fe(II), Ni(II), Co(II), Cu(II), as well as a small amount of Hg(II), $HAsO_2$ and H_3AsO_4. Mn(II) and Fe(II) interfere, because they oxidize more or less rapidly in the air and give precipitates of hydroxide. They are precipitated at the same time as the hydroxides, after the prior addition of a little persulphate or H_2O_2.

A second separation is necessary, which is effected with cyanide. Co and Cu give very stable cobalti- and cuprocyanide complexes from which the sulphides cannot then be precipitated. Hg(II) gives a stable complex, but the sulphide can be precipitated from it. HgS is however soluble in an excess of Na_2S. As_2S_3 and As_2S_5 are also soluble in an excess of sulphide, $Ni(CN)_4^{2-}$ is fairly stable, NiS is not precipitated if there is an excess of cyanide. ZnS and CdS precipitate, because their cyanide complexes are of low stability.

The sensitivity of the precipitation of CdS depends on the concentration of the CN^- which complexes the Cd^{2+}. It is therefore desirable to add the least possible quantity of cyanide, but always sufficient to make sure that NiS does not precipitate. Hence the following procedure.

Procedure.—In a microcone, add 1 drop of conc. NH_3 to 1 drop of the solution under test and, if there is Mn^{2+} present, a crystal of

persulphate. Boil. Add 1 drop of conc. NH$_3$. Centrifuge. Collect the solution in a second test-tube and add 1 drop of cyanide, which gives a precipitate which redissolves. Transfer 1 drop of this solution into 2 drops of sulphide in a microcone. The yellow CdS precipitates. Wait. Centrifuge in order to collect the precipitate and make it more visible.

If a black precipitate comes down, add a further drop of cyanide to the main bulk of the solution, withdraw 1 drop from it for repetition of the test with sulphide.

Concentration limit.—10^{-3} g.-ion of Cd^{2+} per litre. A large excess of cyanide diminishes the sensitivity.

Interfering substances.—The reaction is thus specific, but it must not be confused with white ZnS, which also precipitates, 2.10^{-3} g.-ion/litre (200 p.p.m.).

COPPER

Cu = 63·6

States of oxidation.—In the state of oxidation I copper is similar to Ag(I), Tl(I), Au(I). Its ability to exist in the II state classes it with the zinc group. The states I and II are similar to the corresponding states in mercury. III is unstable, but exists in some complexes and an oxide.
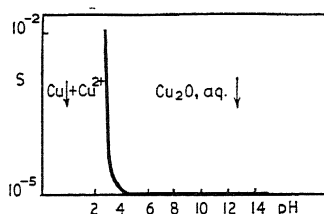
FIG. 57.—APPARENT SOLUBILITY OF Cu(I) HYDROXIDE
AS A FUNCTION OF *p*H

Cu(I)

Influence of *p*H.—The cation Cu$^+$ scarcely exists in solution. The compounds in which Cu has the oxidation number I are all complexes or substances of low solubility. CuOH can exist in solutions of *p*H around 3. It is yellow to orange and rapidly changes to Cu$_2$O. In very acid solution, CuOH disproportionates into Cu ↓ and Cu^{2+}. The properties of the chlorides, cyanides, and sulphates of the three neighbouring elements in column I*b* are similar.

I*b*	II*b*
Cu	Zn
Ag	Cd
Au	Hg

Low-solubility compounds.—The majority of cuprous salts are in this category, and are white: CuCN, CuCl, CuBr, CuCNS, CuI; black Cu$_2$S is completely precipitated in 6N-HCl. It is redissolved in conc. HCl (forming complexes).

Complexes.—Numerous complexes with Cl$^-$, CN$^-$, NH$_3$, S$_2$O$_3{}^{2-}$. They are easily destroyed due to the precipitation of compounds whose

solubility is low. The complex cyanide, on the other hand, is very stable: Cu_2S (and CuS) dissolve in CN^-.

Equilibrium constants

$$\tfrac{1}{2}Cu_2O \downarrow + \tfrac{1}{2}H_2O \rightleftharpoons Cu^+ + OH^- \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ 14 \cdot 9$$

$$CuCl_3{}^{2-} \rightleftharpoons CuCl_2{}^- + Cl^-; \quad pk_3 = -3 \cdot 7; \quad pk_2 = -2 \cdot 0;$$
$$pk_1 = 6 \cdot 7; \quad CuCl \downarrow$$

$$CuBr_2{}^- \rightleftharpoons CuBr \downarrow + Br^-; \quad pk_2 = -2 \cdot 3, \ -3 \cdot 3; \quad pk_1 = 8 \cdot 3$$

$$CuI_2{}^- \rightleftharpoons CuI \downarrow + I^-; \quad pk_2 = -3 \cdot 1, \ -4 \cdot 0; \quad pk_1 = 12 \cdot 0$$

$$Cu(CNS)_4{}^{3-} \rightleftharpoons CuCNS \downarrow + 3CNS^-; pk_2 = -4 \cdot 3, \ -6 \cdot 0; pk_1 = 13 \cdot 4, 15 \cdot 0$$

$$Cu(CN)_3{}^- \rightleftharpoons Cu(CN)_2{}^- + CN^-; \quad pk_3 = 11 \cdot 3; \quad pk_2 = 4 \cdot 2;$$
$$CuCN \downarrow; \quad pk_1 = 19 \cdot 5$$

$$Cu(NH_3)_2{}^+ \rightleftharpoons CuNH_3{}^+ + NH_3; \quad pk_2 = 4 \cdot 9; \quad pk_1 = 5 \cdot 4, 5 \cdot 9$$

$$Cu_2S \downarrow \ \rightleftharpoons 2Cu^+ + S^{2-} \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ 49 \cdot 6$$
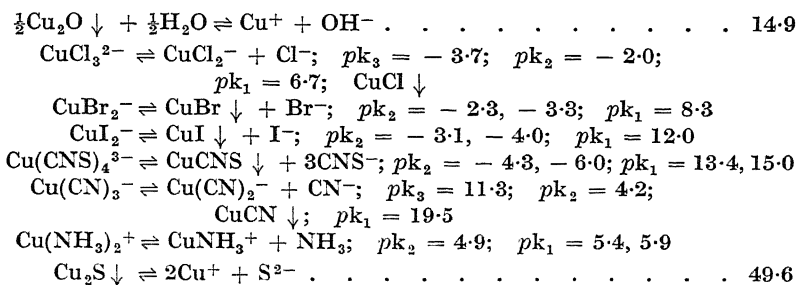
Cu(II)

Influence of pH.—The cation Cu^{2+} is pale blue. $Cu(OH)_2$, pale blue, becomes black on heating, because of dehydration. It precipitates at pH $5 \cdot 0$ ($0 \cdot 01M$), but in the majority of cases, basic salts or adsorption compounds are obtained which are also pale blue and which do not transform into the hydroxide unless the solution is more alkaline.

$Cu(OH)_2$ dissolves to a small extent in extremely alkaline solution giving blue anions $CuO_2{}^{2-}$.
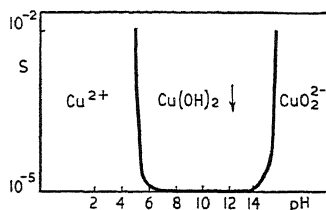
FIG. 58.—APPARENT SOLUBILITY OF $Cu(II)$ HYDROXIDE
AS A FUNCTION OF pH

Complexes.—There are many, blue, yellow, green or brown. $CuCl^+$ and $CuCl_2$ are yellow. The ammine complexes are intense blue. The complexes with CNS^- are brown; those with CN^- are of low stability, destroyed by reduction. Fairly stable blue compounds are formed with hydroxylated organic compounds. The complexes with $CO_3{}^{2-}$ are very unstable.

Low-solubility compounds.—Numerous salts have a low solubility. The least soluble is the ferrocyanide (reddish brown) of low solubility in fairly weak acid; the black sulphide has a low solubility in N-HCl. CuS oxidizes slowly in the air. It dissolves slightly in ammonium sulphide, probably with the formation of ammine complexes. CuS also dissolves in cyanide with the formation of cuprocyanides, and it dissolves slightly in the polysulphides, yielding $CuS_2{}^{2-}$. It is completely precipitated in 6N-HCl and redissolves in conc. HCl.

Equilibrium constants

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+ \quad \ldots \quad 8 \cdot 0$$
$$2Cu^{2+} + H_2O \rightleftharpoons Cu_2OH^{3+} + H^+ \quad \ldots \quad 6 \cdot 8$$
$$2Cu^{2+} + H_2O \rightleftharpoons Cu_2O^{2+} + 2H^+ \quad \ldots \quad 10 \cdot 9$$
$$Cu(OH)_2 \downarrow \; \rightleftharpoons Cu^{2+} + 2OH^- \quad \ldots \quad 17 \cdot 7 - 20 \cdot 0$$
$$Cu(OH)_2 \downarrow \; \rightleftharpoons CuO_2H^- + H^+ \quad \ldots \quad 19$$
$$CuO_2H^- \rightleftharpoons CuO_2{}^{2-} + H^+ \quad \ldots \quad 13 \cdot 1$$
$$CuCl_4{}^{2-} \rightleftharpoons CuCl_3{}^- + Cl^-; \quad pk_4 = -2 \cdot 2; \quad pk_3 = -1 \cdot 5;$$
$$pk_2 = -0 \cdot 7; \quad pk_1 = -0 \cdot 2$$
$$CuBr^+ \rightleftharpoons Cu^{2+} + Br^- \quad \ldots \quad 0 \cdot 0$$
$$Cu(CN)_4{}^{2-} \rightleftharpoons Cu^{2+} + 4CN^- \quad \ldots \quad 27 \cdot 3$$
$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4{}^{2-} \quad \ldots \quad -1 \cdot 0 \text{ for } I = 1$$
$$CuP_2O_7{}^{2-} \rightleftharpoons Cu^{2+} + P_2O_7{}^{4-} \quad \ldots \quad 13 \cdot 2$$
$$Cu(tart.)^+ \rightleftharpoons Cu^{2+} + (tart.)^- \quad \ldots \quad 2 \cdot 2$$
$$Cu(NO_2)_3{}^- \rightleftharpoons Cu(NO_2)_2 + NO_2{}^-; \quad pk_3 = -1 \cdot 0;$$
$$pk_2 = -1 \cdot 0; \quad pk_1 = 1 \cdot 2$$
$$Cu(NH_3)_5{}^{2+} \rightleftharpoons Cu(NH_3)_4{}^{2+} + NH_3; \quad pk_5 = -0 \cdot 5;$$
$$pk_4 = 2 \cdot 0; \quad pk_3 = 2 \cdot 7; \quad pk_2 = 3 \cdot 3;$$
$$pk_1 = 4 \cdot 0$$
$$Cu(IO_3)_2 \downarrow \; \rightleftharpoons Cu^{2+} + 2IO_3{}^- \quad \ldots \quad 7 \cdot 1; \; 6 \cdot 9$$
$$CuCO_3 \downarrow \; \rightleftharpoons Cu^{2+} + CO_3{}^{2-} \quad \ldots \quad 9 \cdot 9$$
$$Cu(C_2O_4)_2{}^{2-} \rightleftharpoons CuC_2O_4 \downarrow \; + C_2O_4{}^{2-}; \quad pk_2 = 2 \cdot 8; \quad pk_1 = 7 \cdot 5$$
$$CuS \downarrow \; \rightleftharpoons Cu^{2+} + S^{2-} \quad \ldots \quad 44 \cdot 1$$
$$Cu \; cupferron_2 \downarrow \; \rightleftharpoons Cu^{2+} + 2 \; cupferron^- \quad \ldots \quad 16 \cdot 0$$
$$Cu \; oxine_2 \downarrow \; \rightleftharpoons Cu^{2+} + 2 \; oxine^- \quad \ldots \quad 23 \cdot 4$$

Redox

$$Cu \downarrow \; - e \rightleftharpoons Cu^+ \quad E_0 = 0 \cdot 52 \text{ volt}$$
$$Cu^+ - e \rightleftharpoons Cu^{2+} \quad E_0 = 0 \cdot 17 \text{ ,,}$$
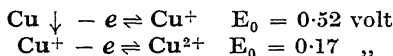
We have seen (p. 92) that Cu^+ disproportionates:

$$|\,Cu^{2+}\,|\,/|\,Cu^+\,|^2 = 10^6$$

The redox system is thus

$$Cu \downarrow \; - 2e \rightleftharpoons Cu^{2+} \quad E_0 = 0 \cdot 35 \text{ volt}$$
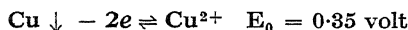
The metal is attacked very slowly by strong acids, for example by dilute H_2SO_4, in the presence of air:

$$2Cu \downarrow \; + 4H^+ + O_2 \uparrow \; \longrightarrow 2Cu^{2+} + 2H_2O$$
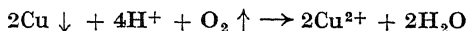
Oxidizing acids attack it very rapidly, nitric acid with formation of NO, hot conc. sulphuric acid with formation of SO_2. Copper salts are reduced to the metallic state by numerous reductants: phosphorous acid, Ti(III), V(II), hydrosulphites, Al, Fe, Zn, Cd, etc.

Formal potentials.—In HCl, Cu(II) complexes: $CuCl_4{}^{2-}$, $CuCl_3{}^-$, $CuCl_2$, $CuCl^+$, and complexes and low-solubility compounds of Cu(I): $CuCl_3{}^{2-}$, $CuCl_2{}^-$, $CuCl \downarrow$, are formed.

Typical redox systems are

$$Cu \downarrow \; + Cl^- - e \rightleftharpoons CuCl \downarrow \qquad E_0 = 0 \cdot 12 \text{ volt}$$
$$CuCl \downarrow \; - e \rightleftharpoons Cu^{2+} + Cl^- \quad E_0 = 0 \cdot 57 \text{ ,,}$$
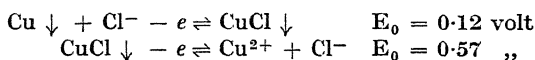
or $\qquad$ $CuCl \downarrow + Cl^- - e \rightleftharpoons CuCl_2 \quad E_0 = 0.62$ volt etc.

The formal potentials for the main systems, as a function of $- \log Cl^-$, are shown in fig. 60.

There are numerous systems in ammoniacal solution.

Cupric salts are poor oxidants, but they are reduced when cuprous salts of low solubility can be formed.

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI \downarrow + I_2$$
$$2Cu(CN)_2 \longrightarrow 2Cu(CN) \downarrow + (CN)_2$$
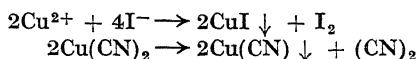
Deep brown $Cu(CNS)_2$ is reduced by sulphites with formation of low-solubility CuCNS (white). The reaction in any case proceeds at a slow rate even when no reductant is present.

$$6Cu(CNS)_2 + 4H_2O \longrightarrow 6CuCNS \downarrow + SO_4{}^{2-} + HCN + 5CNS^- + 7H^+$$
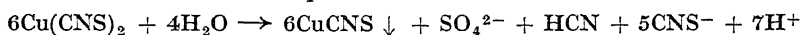
Inversely, the cuprous compounds can be oxidized in the air, $CuCl_2^-$ for example.

In alkaline solution saturated with oxides, the following are the formal potentials:

$$2Cu \downarrow - 2e + 2OH^- \rightleftharpoons Cu_2O \downarrow + H_2O \quad -0.36 \text{ volt } (pH\ 14)$$
$$Cu_2O \downarrow - 2e + 2OH^- + H_2O \rightleftharpoons 2Cu(OH)_2 \downarrow \quad . \quad -0.09 \quad ,, \quad (pH\ 14)$$

$Cu(OH)_2$ can be oxidized to yellow Cu_2O_3, 0.50 to 0.65 volt at pH 14.

$$Cu \downarrow - e + 2NH_3 \rightleftharpoons Cu(NH_3)_2{}^+ \quad E_0 = -0.11 \text{ volt}$$
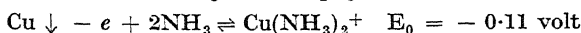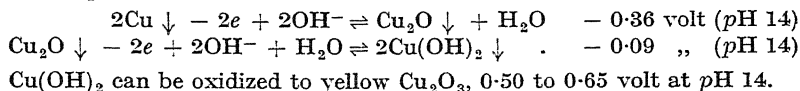
Copper is oxidized by the air in the presence of ammonia, and oxidation goes as far as the formation of the complex $Cu(NH_3)^{2+}$.

In cyanide solution:

$$Cu \downarrow + 2CN^- - e \rightleftharpoons Cu(CN)_2{}^-$$

and

$$Cu \downarrow + 3CN^- - e \rightleftharpoons Cu(CN)_3{}^{2-} \quad -1.0 \text{ volt in 7M-KCN}$$
$$Cu^{2+} + 3CN^- + e \rightleftharpoons Cu(CN)_3{}^-$$
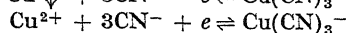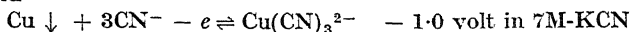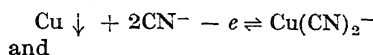
$$E = 1.34 + 0.06 \log \frac{|\ Cu^{2+}\ |.|\ CN^-\ |^3}{|\ Cu(CN)_3{}^{2+}\ |} \text{ volts}$$
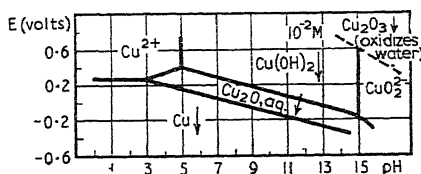
FIG. 59.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF COPPER AS A FUNCTION OF pH

The cupricyanide is spontaneously reduced to the much less ionized cuprocyanide:

$$2Cu(CN)_3{}^- + CN^- + H_2O \longrightarrow 2Cu(CN)_3{}^{2-} + CNO^- + 2H^+$$
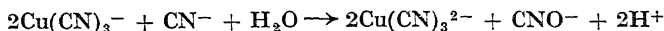
Disproportionations.—In fig. 59 it will be seen that there is no high concentration of Cu^+ in strong acid. What is really striking here is that CuOH is less soluble than $Cu(OH)_2$. It is by this phenomenon that disproportionation is avoided and CuOH can exist.

In fig. 60, it will be seen that the formation of low-solubility CuCl and of $CuCl_2^-$ stabilizes the element in the I oxidation state and impedes its disproportionation.
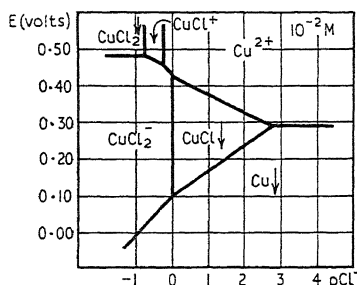
FIG. 60.—APPROXIMATE FORMAL NORMAL POTENTIALS FOR THE REDOX SYSTEMS OF COPPER AS A FUNCTION OF $-\log|Cl^-|$

Detection

(1) **Ammonia.**—Blue coloration due to the formation of ammine complexes.

Concentration limit.—10^{-3} g.-ion of Cu^{2+} per litre, or 60 p.p.m.

Interfering substances.—Ni^{2+} gives the same coloration. Numerous ammine complexes give interfering colorations: Co^{2+}, etc. The precipitate of hydroxides, which are of low solubility in ammonia, in general occludes small quantities of Cu^{2+}.

(2) **Mercurithiocyanate** (see p. 187).—In neutral or slightly acid solution, copper salts in the presence of zinc salts give a pale violet to deep violet precipitate of the mixed mercurithiocyanates of the two elements. This only occurs over a certain range of $|Zn^{2+}|/|Cu^{2+}|$.

The reaction can also be used for the detection of Co(II) and Zn(II) (*q.v.*).

Solutions required.—(1) Solution of ammonium mercurithiocyanate:

Mercuric chloride	30 g
Ammonium thiocyanate	33 g
Water	100 ml
Warm to promote solution.	

(2) Solution of $ZnCl_2$, 0·1 per cent.

Procedure.—To one drop of solution add 1 drop of the zinc solution, then 2 drops of the reagent. Wait.

Concentration limit.—10^{-4} g.-ion of Cu^{2+} per litre, or 6 p.p.m.

Interfering substances.—If there is too large a concentration of Cu^{2+} in the solution, a precipitate of copper mercurithiocyanate comes down. Repeat the test after diluting the solution.

If there is a large proportion of Co^{2+}, the formation of a blue precipitate of cobalt mercurithiocyanate can interfere. Repeat the test after dilution. If the amount of Co(II) is really too large, convert it to the cobaltiammine state by adding 1 drop of 5-vol. H_2O_2 and 1 drop

of 1/1 ammonia. Reacidify with 2 drops of 4N-HCl, and repeat the test immediately.

Fe^{3+}, which gives a red coloration with free CNS^-, can give a violet colour to the precipitate of zinc mercurithiocyanate by adsorption. It must be complexed, before test, with a little solid NaF.

If, however, Fe^{2+} is simultaneously present, it will become a strong reductant on account of the presence of F^- ions, and will reduce Cu^{2+}. It is then necessary, if it is desired to complex Fe^{3+}, to oxidize the Fe^{2+} to the same state beforehand, by adding a crystal of persulphate, the excess of which is destroyed by boiling.

V(IV), if very concentrated, should also be oxidized beforehand.

15

LEAD. BISMUTH. MERCURY

GENERAL PROPERTIES OF THE ELEMENTS WHOSE SULPHIDES ARE OF LOW SOLUBILITY

THEY belong in general to the b sub-groups of the periodic table.

I	II	III	IV	V	VI	VII
Cu(I)	Zn(II)	Ga(III)	Ge(IV)	As(V)	Se(VI)	Br
Ag(I)	Cd(II)	In(III)	Sn(IV)	Sb(V)	Te(VI)	I(VII)
Au(I)	Hg(II)	Tl(III)	Pb(IV)	Bi(V)		

The cations, in general, increase in acidity in the direction of the arrows.

Note.—The analogies between the elements are closer in the first and second lines: Cu(I)–Ag(I), Zn(II)–Cd(II), Ga(III)–In(III), Ge(IV)–Sn(IV), As(V)–Sb(V), Se(VI)–Te(VI).

The same remarks can be applied to the lower states of oxidation.

Ga(I)	Ge(II)	As(III)	Se(IV)	Bi(V)
In(I)	Sn(II)	Sb(III)	Te(IV)	I(V)
Tl(I)	Pb(II)	Bi(III)		

LEAD

$$Pb = 207 \cdot 2$$

States of oxidation.—The most important are II and IV.

Pb(II)

Influence of pH.—The cation Pb^{2+} is colourless. The white hydroxide $Pb(OH)_2$ is amphoteric: it precipitates at pH 7·1 (0·01M) and redissolves at above pH 13·0 to yield the anions PbO_2^{2-} and $HPbO_2^-$. The oxide PbO can be red or yellow.

The basic salts (e.g. PbOHCl, acetates and nitrates) precipitate during the neutralization.

Complexes.—There are not many of these. No stable ammines (distinction from Ag^+, Cu^+, Cu^{2+}, Cd^{2+}, etc.). Unstable complexes: $PbNO_3^+$, $PbCl^+$, $PbCl_2$, $PbCl_3^-$, PbI_3^-, $Pb(CN)_4^{2-}$, etc. Fairly stable acetate, thiosulphate, hydroxylated organic compound complexes.
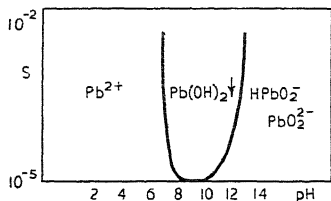
FIG. 61.—APPARENT SOLUBILITY OF Pb(II) HYDROXIDE AS A FUNCTION OF pH

Low-solubility compounds.—The solubility of the majority of the salts is low. $PbCl_2$, $PbBr_2$, yellow PbI_2, more soluble in the hot, crystallizing in shining plates on cooling. PbF_2, $PbSO_4$, the latter dissolves in a large excess of acetate ions whence Pb(II) can be reprecipitated by the addition of acid, SO_4^{2-} or CrO_4^{2-} ions. The least-soluble salts are the yellow chromate and the white phosphate, the solubility of both of which is low in 2N acetic acid, and the black sulphide, whose solubility in 2N-HCl is low. All these compounds, with the exception of the sulphide, dissolve in 2N-NaOH. PbS is slightly soluble in 1·5N-HCl, and dissolves rapidly in 4N-HCl (complex formation). Hydrogen sulphide in dilute hydrochloric acid gives at first a red sulphochloride, then black PbS. PbS is oxidized by HNO_3.

Equilibrium constants

$$PbCl_2 \downarrow \rightleftharpoons Pb^{2+} + 2Cl^- \qquad\qquad 3\cdot7$$
$$PbCl_3^- \rightleftharpoons PbCl_2 + Cl^- \qquad\qquad - \quad 1\cdot8$$
$$PbCl_2 \rightleftharpoons PbCl^+ + Cl^- \qquad\qquad \sim \quad 1\cdot1$$
$$PbCl^+ \rightleftharpoons Pb^{2+} + Cl^- \qquad\qquad 1\cdot1;\ 1\cdot6$$
$$PbBrO_3 \downarrow \rightleftharpoons Pb^{2+} + BrO_3^- \qquad\qquad 1\cdot7$$
$$PbBr_2 \downarrow \rightleftharpoons Pb^{2+} + 2Br^- \qquad\qquad 5\cdot2$$
$$PbBr^+ \rightleftharpoons Pb^{2+} + Br^- \qquad\qquad 1\cdot1$$
$$PbF_2 \downarrow \rightleftharpoons Pb^{2+} + 2F^- \qquad\qquad 7\cdot4$$
$$PbI_2 \downarrow \rightleftharpoons Pb^{2+} + 2I^- \qquad\qquad 7\cdot9$$
$$PbI_3^- \rightleftharpoons Pb^{2+} + 3I^- \qquad\qquad 5\cdot4;\ 6\cdot3$$
$$PbI^+ \rightleftharpoons Pb^{2+} + I^- \qquad\qquad 1\cdot5$$
$$PbSO_4 \downarrow \rightleftharpoons Pb^{2+} + SO_4^{2-} \qquad\qquad 7\cdot7$$
$$Pb(CN)_4^{2-} \rightleftharpoons Pb^{2+} + 4CN^- \qquad\qquad 10\cdot3$$
$$PbC_2O_4 \downarrow \rightleftharpoons Pb^{2+} + C_2O_4^{2-} \qquad\qquad 10\cdot5$$
$$PbHPO_4 \downarrow \rightleftharpoons Pb^{2+} + HPO_4^{2-} \qquad\qquad 10\text{--}11\cdot4$$
$$Pb(IO_3)_2 \downarrow \rightleftharpoons Pb^{2+} + 2IO_3^- \qquad\qquad 12\cdot5$$
$$PbCO_3 \downarrow \rightleftharpoons Pb^{2+} + CO_3^{2-} \qquad\qquad 12\cdot8$$
$$PbCrO_4 \downarrow \rightleftharpoons Pb^{2+} + CrO_4^{2-} \qquad\qquad 13\cdot7$$
$$Pb(OH)_2 \downarrow \rightleftharpoons Pb^{2+} + 2OH^- \qquad\qquad 15\cdot6$$
$$Pb(OH)_2 \downarrow \rightleftharpoons HPbO_2^- + H^+ \qquad\qquad 15$$
$$Pb_3(PO_4)_2 \downarrow \rightleftharpoons 3Pb^{2+} + 2PO_4^{3-} \qquad\qquad 32\cdot0$$
$$PbS \downarrow \rightleftharpoons Pb^{2+} + S^{2-} \qquad\qquad 29$$
$$Pb(CH_3COO)_4^{2-} \rightleftharpoons Pb(CH_3COO)_3^- + CH_3COO^-;\quad pk_4 = 0\cdot5;$$
$$pk_3 + pk_2 = 0\cdot2;\quad pk_1 = 1\cdot4,\ 2\cdot2$$
$$Pb(S_2O_2)_3^{4-} \rightleftharpoons Pb(S_2O_3)_2^{2-} + S_2O_3^{2-};\quad pk_3 = 1\cdot2;$$
$$pk_2 + pk_1 = 5\cdot1$$
$$PbS_2O_3 \downarrow \rightleftharpoons Pb^{2+} + S_2O_3^{2-} \qquad\qquad 6\cdot4$$
$$Pb(CNS)_6^{4-} \rightleftharpoons Pb^{2+} + 6CNS^- \qquad\qquad - \quad 0\cdot3$$
$$Pb(CNS)_2 \downarrow \rightleftharpoons Pb^{2+} + 2CNS^- \qquad\qquad 4\cdot7$$

Pb(IV)

Influence of pH.—The cation Pb^{4+} is very acid and scarcely exists in solution, even when it is very acid. PbO_2, brown (the depth of shade varies), is formed. The hydroxide redissolves in dilute caustic soda giving $Pb(OH)_6^{2-}$ or PbO_3^{2-}.

Complexes.—In concentrated HCl or fairly concentrated H_2SO_4, complexes are formed. E.g. $PbCl_6^{2-}$, $PbCl_5^-$.
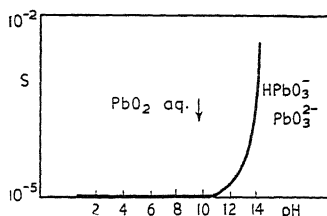
FIG. 62.—APPARENT SOLUBILITY OF $Pb(IV)$ HYDROXIDE
AS A FUNCTION OF pH

Equilibrium constants

$$Pb(OH)_4 \downarrow \rightleftharpoons Pb^{4+} + 4OH^- \quad . \quad . \quad . \quad . \quad . \quad 65\cdot5$$
$$Pb_3O_4 \downarrow \rightleftharpoons PbO_4^{4-} + 2Pb^{2+} \quad . \quad . \quad . \quad . \quad 50\cdot3$$

Redox

(1) $\qquad Pb \downarrow - 2e \rightleftharpoons Pb^{2+} \quad E_0 = -0\cdot13$ volt (slow)
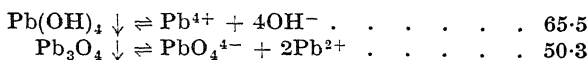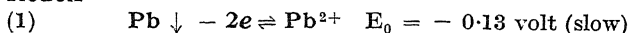
Lead is attacked by nitric acid and by hot concentrated sulphuric acid which dissolves the $PbSO_4$ formed. It is gradually attacked by HCl and concentrated HI with the formation of complexes. HF has no action.

$Pb \downarrow + 2OH^- - 2e \rightleftharpoons PbO_2^{2-} + 2H^+ \quad . \quad . \quad -0\cdot60$ volt (N-KOH)

(2) $\qquad Pb^{4+} + 2e \rightleftharpoons Pb^{2+} \quad E_0 = 1\cdot75$ volts
$$PbO_2 \downarrow + 4H^+ + 2e \rightleftharpoons Pb^{2+} \quad E_0 = 1\cdot47 \quad ,,$$
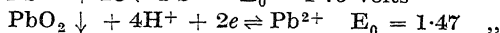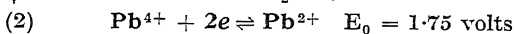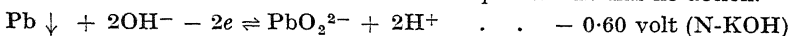
in solution saturated with PbO_2 in $6M-H_2SO_4$: $1\cdot7$ volts.

In HCl we have

$$PbCl_2 \downarrow + 3Cl^- - 2e \rightleftharpoons PbCl_5^- \quad E_0 = 1\cdot39 \text{ volts}$$
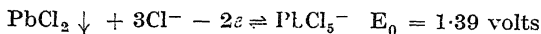
PbO_2 is reduced in acid solution by sulphurous acid, oxalic acid, hot HCl, etc.

In alkaline solution PbO is oxidized to Pb_3O_4 or Pb_2O_3 (which disproportionates very slowly), and PbO_2.

$$Pb_3O_4 \downarrow + H_2O + 2e \rightleftharpoons 3PbO \downarrow + 2OH^- \quad E_0 = 0\cdot25 \text{ volt}$$
$$3PbO_2 \downarrow + 2H_2O + 4e \rightleftharpoons Pb_3O_4 \downarrow + 4OH^- \quad E_0 = 0\cdot32 \quad ,,$$
$$3Pb_2O_3 \downarrow + H_2O + 2e \rightleftharpoons 2Pb_3O_4 \downarrow + 2OH^- \quad E_0 = 0\cdot40 \quad ,,$$
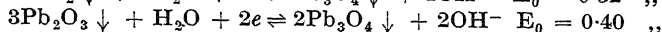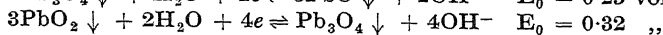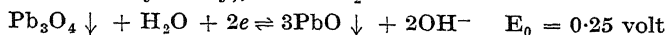
In strongly alkaline solution, PbO_2^{2-} as well as $Pb(OH)_2$ are oxidized by persulphates, hypochlorites, etc. In strongly alkaline solution, PbO_2^{2-} is first oxidized to Pb_2O_3 or Pb_3O_4 which precipitate, then to PbO_3^{2-}.

$$3PbO_2^{2-} + 4H^+ + 2e \rightleftharpoons Pb_3O_4 \downarrow + 2H_2O \quad E = 0\cdot3 \text{ volt}$$
$$Pb_3O_4 \downarrow + 5OH^- - 4e \rightleftharpoons 3PbO_3^{2-} + 5H^+ \quad E = 0\cdot3 \quad ,,$$
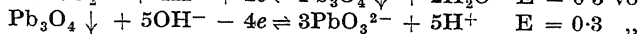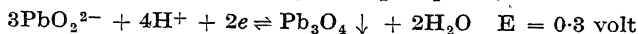
(in N-KOH saturated with the oxides).

Detection

(1) **Precipitation of lead chloride.**—If Pb^{2+} is present in large quantity, $PbCl_2$ is precipitated at the beginning of the analysis. It is soluble in boiling water and crystallizes in white platelets on cooling.

Concentration limit.—10^{-1} to 10^{-2} g.-ion of Pb^{2+} per litre (2⁻20 mg/ml).
Interfering ions.—Ag(I), Hg(I), Tl(I), precipitate under the same con-

ditions. Hg(I) and Tl(I) redissolve in the presence of oxidants such as chlorine water. If Tl(I) and Tl(III) are oxidized by chlorine water and if the precipitate of chlorides is centrifuged at the boil, the crystallization of $PbCl_2$ on cooling is specific.
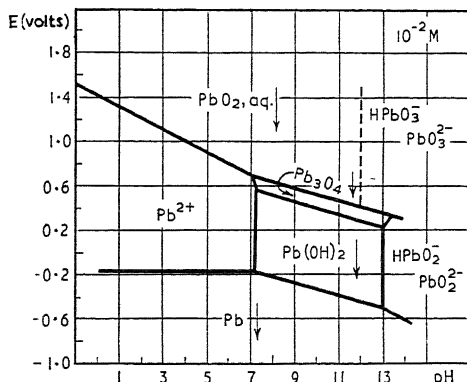
FIG. 63.—APPROXIMATE FORMAL NORMAL POTENTIALS FOR THE REDOX SYSTEMS OF Pb AS A FUNCTION OF pH

(2) **Precipitation as lead sulphide.**—Black lead sulphide cannot be used to characterize lead until after numerous interfering ions have been removed.

Solutions required.—Saturated sodium sulphide.
    4N-NaOH.
    20 per cent KCN.
Procedure.—To separate the interfering ions, add 4 drops of 4N-NaOH to
    1 drop of the solution. Boil. Centrifuge. The solution should be colour-
    less, and if it is not, dilute, boil, and re-centrifuge. Add 1 drop of the
    solution to 1 drop of cyanide, and 1 drop of sulphide. A black pre-
    cipitate indicates lead.
Concentration limit.—In general, after the separation, 10^{-3} g.-ion of Pb^{2+}
    per litre (200 p.p.m.).
Interfering substances.—Tl(I) interferes. It can be previously oxidized to
    Tl(III) before separation. Bi(III) gives the same reaction.

<div align="center">

BISMUTH

Bi $= 209 \cdot 0$

</div>

As	**State of oxidation.**—III in the bismuth salts, IV and V
Sb	in the solid state only.
Bi	

<div align="center">

Bi(III)

</div>

Influence of pH.—At pH 0, the cation Bi^{3+} predominates. In less acid solutions more or less condensed basic ions are formed which can be formally represented as $BiOH^{2+}$, BiO^+, or Bi_2O^{4+}, $Bi_3O_2{}^{5+}$, etc., all colourless. Above pH 2·2, basic salts such as $BiOCl$ can precipitate (analogy wit hSb(III)). In sufficiently alkaline solution, white $Bi(OH)_3$ is

obtained. In the hot, yellow BiOOH is the final product. Bi_2O_3 is yellow to deep brown. In hot concentrated NaOH, there is a slight dissolution of this oxide to yield the anions BiO_2^-.

Complexes.—Tartrate · not very stable (difference from Sb(III) which yields tartrate complexes which are much more stable); no ammines (difference from Cu^{2+}, Ag^+ Cd^{2+}, etc.); $BiCl_4^-$, $BiCl_5^{2-}$, $BiCl_6^{3-}$, $Bi_2Cl_9^{3-}$, etc., complexes with mannitol, with CNS^-, etc., none very stable. More stable complexes with $S_2O_3^{2-}$; with I^-, BiI_5^{2-}, BiI_6^{3-}, etc., orange. Citrate and oxalate complexes are known.

Low-solubility compounds.—The white phosphate $BiPO_4$ has a low solubility in 2N-HNO_3, but is soluble in 2N-HCl (complexes). Black BiI_3 and orange BiOI. Bi_2S_3 brownish black. The orange chromate and dichromate have a low solubility in 2N acetic acid. The solubilities of the oxalate and iodate are also fairly low.

Organic solvents.—Complex with I^-, soluble in alcohols and esters.

Equilibrium constants

$$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+ \quad \ldots \quad \sim 2$$
$$BiOH^{2+} \rightleftharpoons BiO^+ + H^+ \quad \ldots \quad \sim 2$$
$$BiOCl \downarrow \rightleftharpoons BiO^+ + Cl^- \quad \ldots \quad 8\cdot2\text{-}9\cdot2$$
$$BiCl_4^- + H_2O \rightleftharpoons BiOCl \downarrow + 3Cl^- + 2H^+ \quad \ldots \quad 0\cdot1$$
$$Bi(OH)_3 \downarrow \rightleftharpoons Bi^{3+} + 3OH^- \quad \ldots \quad 30$$
$$BiOOH \downarrow \rightleftharpoons BiO^+ + OH^- \quad \ldots \quad 12;11$$
$$BiPO_4 \downarrow \rightleftharpoons Bi^{3+} + PO_4^{3-} \quad \ldots \quad 20;19$$
$$Bi_2S_3 \downarrow \rightleftharpoons 2Bi^{3+} + 3S^{2-} \quad \ldots \quad 71\cdot8$$
$$Bi(CNS)_6^{3-} \rightleftharpoons Bi(CNS)_5^{2-} + CNS^-; \quad pk_5 + pk_4 = 0\cdot8;$$
$$pk_4 + pk_3 = 1\cdot2; \quad pk_2 = 1\cdot1; \quad pk_1 = 1\cdot0$$
$$BiONO_3 \downarrow + 2H^+ \rightleftharpoons Bi^{3+} + NO_3^- + H_2O \quad \ldots \quad 2\cdot6$$
$$Bi\text{ cupferron}_3 \downarrow \rightleftharpoons Bi^{3+} + 3\text{ cupferron}^- \quad \ldots \quad 27\cdot3$$
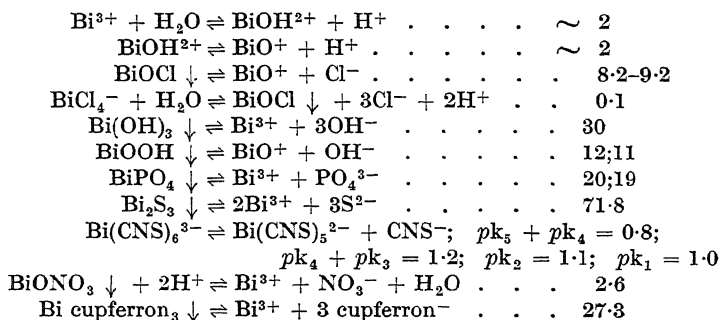
Redox.—(1) $Bi^{3+} + 3e \rightleftharpoons Bi \downarrow \quad E_0 = 0\cdot23$ volt (fairly slow)

In HCl: $BiOCl \downarrow + 2H^+ + 3e \rightleftharpoons Bi \downarrow + H_2O + Cl^-$
$E'_0 = -0\cdot05$ volt in 5N-HCl; $0\cdot0$ volt in N-HCl

In alkaline solution: $Bi_2O_3 \downarrow + 6H^+ + 6e \rightleftharpoons Bi \downarrow + 3H_2O$
$E_0 = -0\cdot41$ volt in N-NaOH saturated with oxides

The metal is thus a relatively poor reductant. It is attacked by concentrated nitric acid and hot concentrated sulphuric acid. Bismuth salts are reduced by metallic tin, by Sn(II) in alkalis, and by Ti(III) in acids.

(2) $HBiO_3 \downarrow + 5H^+ + 2e \rightleftharpoons Bi^{3+} + 3H_2O \quad E \sim 1\cdot7$ volts at pH 0
(calculated)

In alkaline solution, oxidation of BiO_2^- gives successively Bi_4O_7 and then Bi_2O_4, both having low solubility.

$$2Bi_2O_3 \downarrow + H_2O - 2e \rightleftharpoons Bi_4O_7 \downarrow + 2H^+ \quad E = 0\cdot5 \text{ volt}$$
$$Bi_4O_7 \downarrow + H_2O - 2e \rightleftharpoons 2Bi_2O_4 \downarrow + 2H^+ \quad E = 0\cdot6 \text{ ,,}$$

(both in N-NaOH saturated with oxides).

$NaBiO_3$ or Na_3BiO_4, whose solubility is low, is prepared by the action of fused sodium peroxide on Bi_2O_3; by the oxidation of BiO_2^- by hypochlorites or by H_2O_2 in alkaline solution.

Bi(V) oxidizes nearly all the systems in acid solution in the cold. Ce(III) gives Ce(IV), Mn(II) gives MnO_4^-. The excess of oxidant is easy to separate by filtration.

Detection

(1) **Reduction by tin.**—A drop of solution placed on a piece of tin foil gives immediately a black stain of metallic bismuth.

Concentration limit.—5.10^{-4} g.-ion of Bi(III) per litre, or 100 p.p.m.

Interfering ions.—Ag^+, Hg^{2+} and Hg_2^{2+}, Sb(III) give the same reaction. As(III) gives brown-black arsenic slowly, more rapidly in HCl and when the As(III) is concentrated. Mo(VI), W(VI), and V(V) give blue-black oxides, which are precipitated very rapidly in very acid solution.

(2) **Precipitation of bismuth by stannite.**—Bismuth is precipitated as metal by reduction with stannous salts in alkali.

Solutions required.—5 per cent $SnCl_2$ in 2·5N-HCl. 4N-NaOH.

Procedure.—Place a drop of stannous chloride on a spot plate, add 2 drops of caustic soda, stir, then add a drop of the solution under test. If Bi is present, a black precipitate appears immediately, or after a few seconds at the most.

Concentration limit.—5.10^{-4} g.-ion/litre, or 100 p.p.m.

Interfering substances.—(1) The solution should be sufficiently alkaline to avoid the precipitation of black $Sn(OH_2)$. In too alkaline solution, stannous tin disproportionates very slowly, giving a precipitate of tin. Hence stannite is prepared as part of the test.

(2) Mercury gives the same reaction; it is separated by heating, in a small tube on a water bath, 1 drop of the solution, 1 drop of 4N-HCl and powdered antimony; decant and remove 1 drop of the supernatant liquid for test. The sensitivity is not decreased.

Lead precipitates very slowly, but in a saturated solution of $PbCl_2$ the precipitate does not appear for 10–15 minutes; thus it does not interfere. Ag, Au, Te, and metals of the platinum group also precipitate.

Fe(II) is capable of precipitating lead in alkaline solution. It should therefore be oxidized beforehand by a little persulphate, the excess of which is destroyed by boiling for 30 seconds.

(3) The presence of considerable quantities of coloured hydroxides can interfere; CuOH (or Cu_2O), orange, then precipitates but does not prevent the observation of a black precipitate.

MERCURY

Hg = 200·6

States of oxidation.—I$^+$ in which mercurous mercury is similar to cuprous copper, to Hg(I) and Au(I), II$^+$ in which mercuric mercury is similar to copper and lead.

Hg(I)

In the oxidation state I mercury falls into the silver group (see p. 242). **Influence of *p*H.**—The mercurous ion Hg_2^{2+} (condensed ion) is

colourless. From pH 3–4 (0·01M), it ceases to exist as a result of disproportionation into HgO and black mercury. The corresponding hydroxide is not known (fig. 64).

Water causes the precipitation of yellow or brown basic salts.

Low-solubility compounds.—The only soluble ones are the nitrate, the perchlorate, and the acetate. The halides are of very low solubility. Ammonia causes Hg_2Cl_2 to go black as a result of the formation of mercury (disproportionation) (see p. 102).

The chromate is red, the iodide green, the sulphide black; the other salts are white.

Equilibrium constants

$$Hg_2Cl_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2Cl^- \quad . \quad . \quad . \quad . \quad 17·5; \ 18·0; \ 16·9 \ (I = 0·5)$$
$$Hg_2Cl_3^- \rightleftharpoons Hg_2Cl_2 \downarrow + Cl^-$$
$$Hg_2Cl_4^{2-} \rightleftharpoons Hg_2Cl_3^- + Cl^- \quad . \quad . \quad - \ 1$$
$$Hg_2Br_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2Br^- \quad . \quad . \quad . \quad . \quad 21·3 \ (I = 0·5)$$
$$Hg_2I_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2I^- \quad . \quad . \quad . \quad . \quad 23·3; \ 27·9; \ 27·5 \ (I = 0·5)$$
$$Hg_2(IO_3)_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2IO_3^- \quad . \quad . \quad . \quad 18·7; \ 19·5$$
$$Hg_2(CN)_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2CN^- \quad . \quad . \quad . \quad 39; \ 39·3$$
$$Hg_2C_2O_4 \downarrow \rightleftharpoons Hg_2^{2+} + C_2O_4^{2-} \quad . \quad . \quad . \quad 13·0$$
$$Hg_2S \downarrow \rightleftharpoons Hg_2^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad 30; \ 45$$
$$Hg_2(CNS)_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2CNS^- \quad . \quad . \quad . \quad 19·5$$
$$Hg_2CO_3 \downarrow \rightleftharpoons Hg_2^{2+} + CO_3^{2-} \quad . \quad . \quad . \quad 16$$
$$Hg_2SO_4 \downarrow \rightleftharpoons Hg_2^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 6·3$$
$$Hg_2CrO_4 \downarrow \rightleftharpoons Hg_2^{2+} + CrO_4^{2-} \quad . \quad . \quad . \quad 8·7$$

Hg(II)

Influence of pH.—The mercuric cation Hg^{2+} is colourless. Yellow HgO (red in the hot) precipitates at pH 2·0 (0·01M) in a solution not containing complex-forming ions (ClO_4^-). In very strong alkali $HHgO_2^-$ commences to form. When neutralizing there is generally a precipitation of basic salts such as HgOHCl or $HgO,HgCl_2$; the same with SO_4^{2-} and NO_3^-; they are yellow or red. $HgCl_2$ gives a precipitate at pH 7 and $Hg(NO_3)_2$ at pH 2.

Complexes.—They are very numerous and often quite stable: chlorides: $HgCl_2$ in particular is soluble and little ionized; the bromide and iodide complexes are more stable: HgI_4^{2-} in particular; thiocyanates up to $Hg(CNS)_4^{2-}$; very stable cyanides: $Hg(CN)_2$, $Hg(CN)_4^{2-}$.

Ammines of low stability; sulphite and thiosulphate complexes.

Note.—$HgCl_2$ is slightly volatile in water vapour.

Low-solubility compounds.—HgI_2 red, $Hg(CNS)_2$ white, etc. Ammonia causes a precipitation of the very low solubility white compound $HgNH_2Cl$ when it acts on a solution of mercuric chloride, as a result of disproportionation of ammonia: $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$. NH_2^- is a very strong base; the compound is soluble in acids and also in NH_4^+ by displacement of the preceding equilibrium. Basic precipitates can also be obtained: $HgO.HgNH_2NO_3$ white, and $HgO.HgNH_2I$ orange.

The sulphide, generally black, can be obtained in cinnabar red in the dry way. It is not attacked by hot dilute nitric acid or by concentrated HCl. It is one of the least soluble substances met with in qualitative

analysis. In the presence of an excess of sodium sulphide, it dissolves slightly giving HgS_2^{2-}, but does not do so in ammonium sulphide. Passage of hydrogen sulphide into the solution of a mercuric salt in hydrochloric acid can give rise to the formation of a yellowish-white precipitate of the chlorosulphide $Hg_3S_2Cl_2$ whose solubility in concentrated HCl is small; it becomes reddish brown, then black, by the action of H_2S.

Organic solvents.—$HgCl_2$ is soluble in alcohol and in ether. HgI_2 is soluble in alcohol, ether, and benzene.

Equilibrium constants

$$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+ \quad \dots \quad 2\cdot7; \ 2\cdot8$$
$$HgOH^+ + H_2O \rightleftharpoons Hg(OH)_2 + H^+ \quad \dots \quad 3\cdot5$$
$$HgO \downarrow + H_2O \rightleftharpoons Hg^{2+} + 2OH^- \quad \dots \quad 26$$
$$HgS \downarrow \rightleftharpoons Hg^{2+} + S^{2-} \quad \dots \quad 53\cdot5; \ 51\cdot0; \ 52\cdot5$$
$$HgS_2^{2-} \rightleftharpoons Hg^{2+} + 2S^{2-} \quad \dots \quad 54\cdot7$$
$$HgI_4^{2-} \rightleftharpoons HgI_3^- + I^-; \quad pk_4 = 2\cdot2; \quad pk_3 = 3\cdot8; \quad pk_2 = 10\cdot9;$$
$$pk_1 = 12\cdot9 \quad (HgI_2 \ \text{dissolved}; \ I = 0\cdot5; \ 25°);$$
$$pk_1 + pk_2 + pk_3 + pk_4 = 29\cdot8 \ (I = 0\cdot5);$$
$$30\cdot3; \ 30; \ 31$$
$$HgI_2 \downarrow \rightleftharpoons HgI_2 \quad \dots \quad 4\cdot1 \ (I = 0\cdot5)$$
$$HgI_2 \downarrow \rightleftharpoons Hg^{2+} + 2I^- \quad \dots \quad 28\cdot3; \ 25\cdot6$$
$$Hg(CN)_4^{2-} \rightleftharpoons Hg(CN)_3^- + CN^-; \quad pk_4 \sim 3;$$
$$pk_1 + pk_2 + pk_3 + pk_4 = 40\cdot5; \ 41\cdot4$$
$$Hg(CNS)_4^{2-} \rightleftharpoons Hg(CNS)_3^- + CNS^-; \quad pk_4 = 0\cdot6; \quad pk_3 = 1\cdot7;$$
$$pk_2 + pk_1 = 19\cdot7; \ pk_1 + pk_2 + pk_3 + pk_4$$
$$= 22\cdot7; \ 19\cdot3 \ (Hg(CNS)_2 \ \text{dissolved})$$
$$HgCl_4^{2-} \rightleftharpoons HgCl_3^- + Cl^-; \quad pk_4 = 0\cdot8; \ pk_3 = 1\cdot0;$$
$$pk_2 = 6\cdot5; \ pk_1 = 6\cdot7 \ (I = 0\cdot5)$$
$$Hg(NH_3)_4^{2+} \rightleftharpoons Hg(NH_3)_3^{2+} + NH_3; \quad pk_4 = 0\cdot8; \ pk_3 = 1\cdot0;$$
$$pk_2 = 8\cdot7; \ pk_1 = 8\cdot8$$
$$HgBr_4^{2-} \rightleftharpoons HgBr_3^- + Br^-; \quad pk_4 = 1\cdot3; \ pk_3 = 2\cdot4;$$
$$pk_2 = 8\cdot3; \ pk_1 = 9\cdot0 \ (I = 0\cdot5)$$

Redox

$$\mathbf{2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}} \quad \mathbf{E_0 = 0\cdot91 \ volt}$$

In HCl the solubility of Hg_2Cl_2 is low and $HgCl_2$ is little ionized; there are complex ions as well.

$$\mathbf{Hg_2^{2+} + 2e \rightleftharpoons 2Hg} \downarrow \quad \mathbf{E_0 = 0\cdot80 \ volt}$$
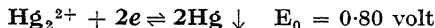
In $4N\text{-}HClO_4$, $E'_0 = 0\cdot66$ volt. In Cl^- it is $0\cdot25$ volt in saturated KCl, $0\cdot28$ volt for M-KCl, $0\cdot33$ for $0\cdot1M$-KCl (calomel electrodes).

Mercury is attacked by oxidants like nitric acid, hot concentrated sulphuric acid and by HI, giving HgI_4^{2-}.

Mercuric salts are easily reduced to the mercurous state and almost as easily to mercury by nearly all metals including copper, by Sn(II), Fe(II), etc. The formation of low-solubility Hg_2Cl_2 favours the halting of the reduction at oxidation state I.

In alkaline solution

$$Hg \downarrow - 2e + 2OH^- \rightleftharpoons HgO \downarrow + H_2O \quad E_0 = 0\cdot15 \ volt$$

in N-NaOH saturated with the oxide.

Disproportionations.—It is seen on fig. 64 that Hg_2O cannot be formed. When the pH becomes sufficiently large Hg_2^{2+} disproportionates into HgO and Hg. In the presence of NH_3, both Hg_2Cl_2 and NH_3 disproportionate:

$$Hg_2Cl_2 \downarrow + 2NH_3 \rightarrow HgNH_2Cl \downarrow + Hg \downarrow + NH_4^+ + Cl^-$$
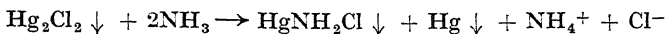
Hg_2S gives $HgS + Hg$.

$Hg_2(CN)_2$ of low stability also gives $Hg(CN)_2 + Hg$.

Hg_2I_2 in the presence of excess of I^- gives $HgI_4^{2-} + Hg$.

Hg_2Cl_2 in concentrated Cl^- in the hot gives $HgCl_4^{2-}$ and Hg.

Only those mercurous compounds whose solubility is very small relative to that of the corresponding mercuric compounds can exist (Table, p. 218).
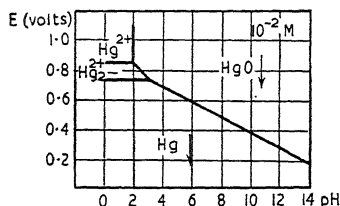
FIG. 64.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF MERCURY IN PERCHLORATE SOLUTION AS A FUNCTION OF pH

Detection

(1) **Reduction to metal.**—A drop of a very acid solution gives a brilliant white stain of amalgam on a piece of polished copper. Wait 1 or 2 seconds, then rub in a stream of water. The amalgam disappears on heating. If the concentration of mercury is high a black precipitate of the very finely divided metal can be obtained. Repeat the operation in more dilute solution.

Concentration limit.—$5 . 10^{-4}$ g.-ion of Hg per litre (100 p.p.m.).

Interfering ions.—Ag^+ sometimes gives a similar precipitate but it is not present in hydrochloric acid solution. As, Sb, Bi come down very slowly as black precipitates. Black precipitates are also given by metals of the platinum group and gold.

(2) **Reduction by stannous chloride.**—In HCl solution a white precipitate of mercurous chloride is first obtained, which is reduced to black mercury by an excess of stannous chloride.

Concentration limit.—10^{-3} g.-ion of Hg per litre (200 p.p.m.).

Interfering substances.—Ag^+ gives black silver. As(III) is reduced in hot 12N-HCl. W(VI) gives deep blue W_2O_5. The precious metals precipitate.

(3) **Action of ammonia on mercurous salts.**—Ammonia gives a black precipitate of metallic mercury with mercurous salts.

$$Hg_2Cl_2 \downarrow + 2NH_3 \rightarrow HgNH_2Cl \downarrow + Hg \downarrow + NH_4^+ + Cl^-$$
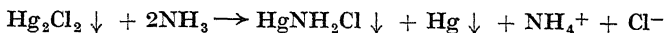
Concentration limit.—$4 . 10^{-4}$ g.-ion of Hg_2^{2+} per litre (200 p.p.m.).

ARSENIC GROUP

ARSENIC. ANTIMONY. TIN (GERMANIUM). VANADIUM. MOLYBDENUM. TUNGSTEN

THE sulphides of this group redissolve in alkaline solution forming anions and also in solutions containing an excess of S^{2-} ions with the formation of sulphide complexes.

The analogies between the different elements permit their classification in two sub-groups:

(1) As(III) and As(V)—Sb(III) and Sb(V)—Sn(IV)—Ge(IV).
(2) Mo(VI)—W(VI)—V(V).

I. ARSENIC—ANTIMONY—TIN—(GERMANIUM)

Common properties.—These can be deduced from their respective positions in the periodic classification. The hydroxides and sulphides give anions.

Pb^{4+} only exists in very small concentration corresponding to the very low solubility of PbO_2. Sn^{4+} is more acid; it scarcely exists. Thus in sulphate and chloride solutions it is present in the form of complexes. SnS_2 has a very low solubility. Sb^{5+} and As^{5+} thus do not exist. As(V) exists in H_3AsO_4 and in As_2S_5, which is very little ionized into ions. $Pb(OH)_2$ is soluble in alkali, giving anions. The same is true of H_2SnO_3; H_3AsO_4 is the most acid and the anions are more stable. On the other

IVb	Vb	VIb
Si(IV)	P(V)	S(VI)
Ge(IV)	As(V)	Se(VI)
Sn(IV)	Sb(V)	Te(VI)
Pb(IV)	Bi(V)	Po(VI)

	P(III)	
Ge(II)	As(III)	Se(IV)
Sn(II)	Sb(III)	Te(IV)
Pb(II)	Bi(III)	
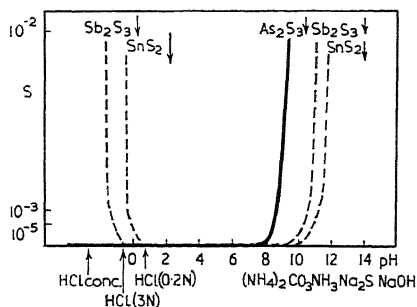
FIG. 65.—APPARENT SOLUBILITY OF THE SULPHIDES OF ARSENIC, ANTIMONY, AND TIN AS A FUNCTION OF pH

hand it is soluble. Ge(IV) is placed between Sn(IV) and As(V). The oxidation number of the other basic oxidation state is less by 2 units. The same rules apply. The cations are less acid than the corresponding

cations of the higher oxidation state. As^{3+} is the most acid and only exists in a very small, very acid region. Apart from Pb^{2+} they are all very acid.

Finally there is a negative oxidation state: $As(III^-)$, $Sb(III^-)$, $Ge(IV^-)$ and $Se(II^-)$, $Te(II^-)$; there are closer analogies between Sn and Ge, and As and Sb.

Solubility of the sulphides.—The solubilities of the sulphides as a function of pH are shown qualitatively in fig. 65.

In acid solution for example:

$$As_2S_3 \downarrow + 3H^+ + 2H_2O \longrightarrow 3H_2S + 2HAsO_2$$

In alkaline solution

$$2As_2S_3 \downarrow + 4OH^- \longrightarrow AsO_2^- + 3AsS_2^- + 2H_2O$$
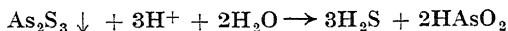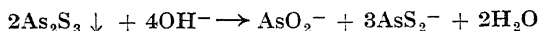
In the presence of an alkaline sulphide

$$As_2S_3 \downarrow + S^{2-} \longrightarrow 2AsS_2^-$$
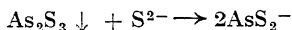
Volatility of chlorides.—$AsCl_3$, $SbCl_3$, $SnCl_4$, $GeCl_4$ are volatile and are lost when the solution in hydrochloric acid is evaporated to dryness.

ARSENIC

As $= 74.9$

States of oxidation.—III^-, III^+, V^+ in which arsenic is very similar to antimony.

IV	V	VI
	P	
Ge	As	Se
	Sb	

As(III⁻). Arsine AsH₃

This is a gas, with a garlic odour, of low solubility and little ionized. As^{3-} is extremely basic.

Arsenides are decomposed by water, with liberation of arsine, except those whose solubility is very low, such as Ag_3As which is black. At $400-500°$ AsH_3 breaks down to arsenic.

As(III)

Influence of pH.—In concentrated acid solution the colourless AsO^+ is present. Then $HAsO_2$, arsenious acid, is formed, colourless and soluble ($0.2M$). Above pH 9.2 only the colourless anion AsO_2^- is present.

Arsenious oxide As_2O_3 is a white solid volatile at $220°$. Its various modifications are fairly soluble in water and only hydrate very slowly to $HAsO_2$; they dissolve in concentrated HCl or in strong alkali.

Low-solubility compounds.—The alkali arsenites are soluble, the others are soluble in acid. Ag_3AsO_3 is yellow. The sulphide As_2S_3, yellow to orange, has a low solubility in hot 6N-HCl and in cold 12N-HCl. It redissolves from pH 7-8. It is often colloidal, flocculated by NH_4^+ and by H^+. It is attacked by oxidants: bromine and hot concentrated nitric acid, giving ions of arsenic acid H_3AsO_4.

AsI_3, orange, has a low solubility. It precipitates in concentrated acid.

Complexes.—In hydrochloric acid, $AsOCl$, $AsOHCl_2$, $AsCl_3$ exist. $AsCl_3$ boils at $130°$ but commences to volatilize at $110°$.

Sulphide complexes are destroyed below pH 8.

Equilibrium constants

$$\text{AsO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{HAsO}_2 + \text{H}^+ \quad . \quad . \quad . \quad - \ 0\cdot3$$
$$\text{HAsO}_2 \rightleftharpoons \text{AsO}_2^- + \text{H}^+ \quad . \quad . \quad . \quad . \quad 9\cdot2$$
$$\text{As}_2\text{S}_3 \downarrow + 4\text{H}_2\text{O} \rightleftharpoons 3\text{H}_2\text{S} + 2\text{HAsO}_2 \quad . \quad . \quad . \quad 22\cdot7$$
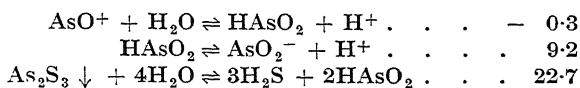
As(V)

The cations scarcely exist; they are strong acids. The ions AsO^{3+} and AsO_2^+, which can only exist in very small concentrations, have been reported. In acid solution arsenic acid H_3AsO_4, colourless and soluble, is formed. In properties it resembles H_3PO_4. Anions corresponding to ortho- and meta-arsenic acids analogous to those of the corresponding phosphoric acids are known (see p. 301). The acidity constants of H_3AsO_4 are $pk_3 = 2\cdot3$; $pk_2 = 4\cdot4\text{--}6\cdot8$; $pk_1 = 9\cdot2\text{--}11\cdot5$.

Complexes.—In particular the tartrate complexes should be mentioned. Also those with Mo(VI), W(VI), etc., complexes such as $\text{H}_7[\text{As}(\text{Mo}_2\text{O}_7)_6]$ whose yellow alkali salts are of low solubility in strong acid; the complex is destroyed in alkaline solutions. Complexes with polyhydric alcohols are formed.

Low-solubility compounds.—The arsenates are analogous to the phosphates. Only the alkali arsenates are soluble; the others are soluble in acid solution. Reddish-brown Ag_3AsO_4 only precipitates in neutral solution. Ammonium magnesium arsenate $\text{MgNH}_4\text{AsO}_4$ is analogous to the phosphate.

Yellow As_2S_5 is obtained by precipitation with hydrogen sulphide from hot, very acid solution, e.g. conc. HCl. Its properties are similar to those of As_2S_3. It is slightly more acid. In less acid solution or in the cold, hydrogen sulphide reduces the arsenate ion extremely slowly, precipitating arsenious sulphide and sulphur. It is for this reason that arsenate solutions are often reduced by SO_2 before precipitating by hydrogen sulphide. It is more convenient in this case to use a little iodide which catalyses the reduction of As(V) by hydrogen sulphide.

Organic solvents.—The arsenimolybdic complexes are soluble in a number of organic solvents, in particular in alcohols.

Equilibrium constants

$$\text{H}_3\text{AsO}_4 \rightleftharpoons \text{H}_2\text{AsO}_4^- + \text{H}^+; \ pk_3 = 2\cdot3; \ pk_2 = 4\cdot4\text{--}6\cdot8; \ pk_1 = 9\cdot2\text{--}11\cdot5$$
$$\text{Ag}_3\text{AsO}_4 \downarrow \rightleftharpoons 3\text{Ag}^+ + \text{AsO}_4^{3-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 22\cdot0$$

Redox.—(1) $\qquad\qquad \text{As} \downarrow + 3\text{H}^+ + 3e \rightleftharpoons \text{AsH}_3 \uparrow$
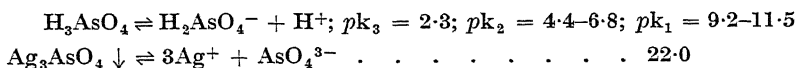
Reduction is effected by zinc in acid.

E_0 calculated $= -\ 0\cdot54$ volt, saturated solution of AsH_3.

$$\text{As} \downarrow + 3\text{H}_2\text{O} + 3e \rightleftharpoons \text{AsH}_3 \uparrow + 3\text{OH}^-; \quad -1\cdot37 \text{ volt (calc.)}$$

(2) $\text{HAsO}_2 + 3\text{H}^+ + 3e \rightleftharpoons \text{As} \downarrow + 2\text{H}_2\text{O} \quad E_0 = 0\cdot25$ volt (slow)
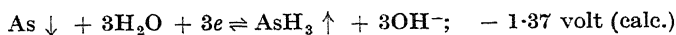
The arsenious salts are reduced in concentrated HCl by Sn(II), and by hypophosphite on the water bath to a brown precipitate of colloidal arsenic (slow reaction). Tin only reduces them very slowly (difference from Sb). Arsenic is attacked by nitric acid finally giving H_3AsO_4.

(3) $As(V) + 2e \rightleftharpoons As(III)$
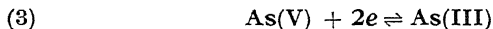
The system is scarcely ever reversible (very slow).

$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$ $E_0 = 0.57$ volt (calc.)
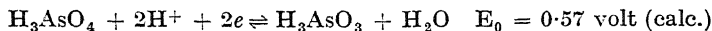
As(V) only oxidizes at a reasonable speed in very acid solution and the reaction is still slow. Some systems catalyse the reaction: I^0/I^-; Re(V)/Re(VII). Sulphurous acid and stannous tin only reduce them in the presence of catalysts. On the other hand, $HAsO_2$ is difficult to oxidize in acid solution; the reactions are very slow even when catalysed.

Formal potentials.—0.58 volt in N-HCl or $HClO_4$.

Above pH 0.5 H_3AsO_4 is only reduced very slowly and only at a reasonable speed with very powerful reductants.

In alkaline solution we have

$AsO_4^{3-} + 4H^+ + 2e \rightleftharpoons AsO_2^- + 2H_2O$ $E_0 = -0.71$ volt (pH 14)
(calc.)
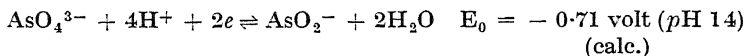
AsO_4^{3-} is only reduced at an infinitely slow rate in alkali.

Formal potentials.—0.07 volt in N-NaOH and -0.16 in 5N-NaOH.

AsO_2^- is oxidized fairly rapidly at pH > 10; less rapidly between pH 10 and pH 6; the concentration of the AsO_2^- ions diminishes, giving place to $HAsO_2$. At pH < 6 the reaction becomes slower. However, certain substances catalyse the process (iodine systems); in the presence of a little iodide the system becomes reversible, as is shown by radioactive indicators.

In strong hydrochloric acid iodides are oxidized to iodine; in alkaline solution iodine oxidizes arsenites (for example in the presence of sodium bicarbonate at pH 8).

Detection

(1) **In the absence of phosphates; molybdate reagent.**—Addition of molybdate reagent in hot acid solution causes the precipitation of yellow ammonium arsenimolybdate $H_4(NH_4)_3[As(Mo_2O_7)_6]$ analogous to ammonium phosphomolybdate.

Solution required.—In 700 ml of water dissolve
            ammonium molybdate, 50 g, and ammonium nitrate, 75 g
      then dilute to a litre with concentrated HNO_3.
Procedure.—Much Cl^- interferes; it can be partially eliminated by boiling a drop of solution with 2 drops of concentrated nitric acid. Add 2 drops of reagent. Transfer to a water bath. Wait 1 or 2 minutes.
Concentration limit.—10^{-3} g.-ion of As per litre (70 p.p.m.).
Interfering substances.—H_3PO_4 gives the same reaction. Si(IV), Ge(IV) give yellow colorations. As(III) is oxidized to As(V) before boiling with HNO_3; the reaction is then obtained.

(2) **Formation of arsine in alkaline solution.**—Compounds of As(III) are reduced by aluminium in alkaline solution to AsH_3; the presence of this is demonstrated with silver nitrate. Compounds of As(V) which cannot be reduced in alkali should be previously reduced in acid.

Solutions required

(1) 4N caustic soda.

(2) Aluminium turnings.

(3) 25 per cent $AgNO_3$.

(4) Pure ground antimony, or bisulphite.

Procedure.—(1) **Compounds of As(III).**—Into a small test-tube introduce a drop of the solution under examination, not very acid, then 2 drops of caustic soda and a small piece of aluminium. Place a small piece of paper impregnated with a drop of silver nitrate over the mouth of the tube. Warm on the water bath. Wait for a minute. The presence of arsenic is indicated by a yellow to black stain.

At the same time a blank test should be made with the same reagent.

(2) **Compounds of As(V).**—Start by reducing them in the initial solution with a few drops of bisulphite or a little antimony powder at the boil. Then carry out the reaction as above (it is unnecessary to separate antimony since it does not interfere).

Note.—Avoid wetting the mouth of the tube with the caustic soda solution as this will give a brown stain of Ag_2O on the paper.

Concentration limit.—10^{-4} g.-ion/litre (10 p.p.m.).

Same limit for the compounds of As(V) after reduction.

Interfering substances.—NH_4^+, which gives a yellow stain, must be absent; remove it with caustic soda until a negative reaction to Nessler solution is obtained (p. 140). PH_3 and H_2S give the same reactions, but the phosphates, sulphates, sulphite are not reduced and thus do not interfere. No other metal gives an analogous reaction. Sb(III) is reduced to metal and does not interfere so long as the solution is not heated for too long. (Confirm, by a blank test made in the presence of antimony, that the operation is being carried out correctly.) On the other hand, when the reduction is made in acid solution Sb(III) gives SbH_3 and interferes.

Reducible compounds can interfere by delaying the reduction of As(III). Cu(II) in the proportion of 100/1 lowers the concentration limit to 10^{-3} g.-ion/litre; in addition the reaction is slowed down; wait at least 5 minutes. The sensitivity is much reduced by Hg(II), because it produces with AsH_3 a compound similar to that with silver; when this element is present the initial acid solution is treated with a little antimony powder; metallic mercury precipitates and does not interfere further. Under these conditions the concentration limit of the reaction is not lowered when mercury is present in the proportion of 1000/1.

Other metals do not interfere even when present in the ratio of 1000/1.

ANTIMONY

$$Sb = 121 \cdot 8$$

States of oxidation.—III$^-$, III$^+$, V$^+$, IV$^+$ of little importance.

Sb(III$^-$)

Stibine, SbH_3, has almost the same properties as AsH_3. It is a little less stable. With silver salts a black precipitate of Ag_3Sb is obtained.

Sb(III)

Influence of pH.—White $HSbO_2$ has a low solubility. It is dissolved to the extent of $10^{-6}M$ as SbO^+ in N-$HClO_4$; it dissolves in hydrochloric acid forming complexes.

In general, in very weak acid, a basic salt is precipitated; $SbOCl$, antimonyl chloride (similarity to bismuth), below 4N-HCl.

From pH 10–11, colourless SbO_2^- is present.

Low-solubility compounds.—The sulphide Sb_2S_3 varies in colour from yellow to orange and to black depending on its particle size. It is

yellow when colloidal, black when it is precipitated hot from very acid solution such as 3N-HCl. It dissolves slowly in hot concentrated hydrochloric acid. In alkalis it redissolves from pH 10; its solubility in ammonium carbonate is thus low (difference from arsenic), but it dissolves in ammonium sulphide. $SbOS_2$ is red. The red iodide SbI_3 precipitates in acid solution.

FIG. 66.—APPARENT SOLUBILITY OF Sb(III) HYDROXIDE AS A FUNCTION OF pH IN $HClO_4$

Complexes.—Chloride complexes; $SbCl_3$ distils at 225°, but volatilizes markedly at 130° and above. Low-stability sulphate complexes. Numerous complexes with SbO^+: tartrate, SbO tart.$^-$; oxalates. The tartrate complex is fairly stable since $SbOCl$ does not precipitate below pH 3 (difference from Bi(III)), and $HSbO_2$ does not precipitate at pH 8. Fluoride complexes. All these complexes are destroyed by precipitation of the sulphide. Sulphide complexes. SbS_3^{3-}, SbS_2^{2-}, $SbOS^-$.

Equilibrium constants

$$\tfrac{1}{2}Sb_2O_3 \downarrow\; + \tfrac{1}{2}H_2O \rightleftharpoons SbO^+ + OH^- \quad . \quad . \quad . \quad . \quad 17$$
$$HSbO_2 \downarrow\; \rightleftharpoons SbO_2^- + H^+ \quad . \quad . \quad . \quad . \quad 10\text{–}11$$
$$Sb_2S_3 \downarrow\; + H_2O + 2H^+ \rightleftharpoons 2SbO^+ + 3H_2S \quad . \quad . \quad . \quad . \quad 30$$
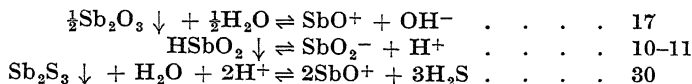
Sb(V)

Few known differences from Sb(III). $HSbO_3$ or H_3SbO_4 is of low solubility even in conc. HNO_3. Chloride complexes, whence SbO_2Cl, low solubility and white, reprecipitates even in quite acid solution. In alkaline solution $Sb(OH)_6^-$ or SbO_3^- is present. Silver antimoniate has a low solubility. Orange Sb_2S_5, if it exists, is similar to Sb_2S_3.

Complexes.—Chloride and sulphate. Fluoride complexes are very stable, the sulphide and hydroxide cannot be precipitated from them. Sulphide complexes; SbS_4^{2-}, SbO_3S^{3-} analogous to complexes with Sb(III). Tartrate complexes, probably containing SbO_2^+. In conc. HCl Sb(IV) complexes occur.

Redox

(1) $\quad Sb \downarrow + 3H^+ + 3e \rightleftharpoons SbH_3 \uparrow \quad . \quad . \quad . \quad . \quad -0.5$ volt (calc.)

$\quad\quad Sb \downarrow + 3H_2O + 3e \rightleftharpoons SbH_3 \uparrow + 3OH^- \quad . \quad -1.3$,,
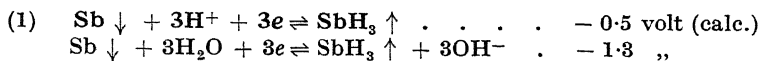
(Solutions saturated with SbH_3.)

The potentials are very little different from those for arsenic. However, the reduction of Sb to SbH_3 is very slow, particularly in cold alkali (difference from As).

(2) $\quad SbO^+ + 2H^+ + 3e \rightleftharpoons Sb \downarrow + H_2O$ . . . . . 0·21 volt

or $\qquad\qquad Sb^{3+} + 3e \rightleftharpoons Sb \downarrow$ . . . . 0·10 ,,
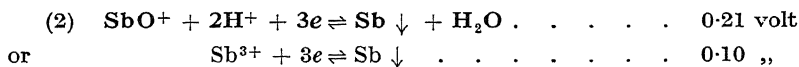
Formal potentials

$$\begin{array}{lll}
0\cdot2\text{–}1N\text{-}HClO_4 & E'_0 = & -\ 0\cdot15 \text{ volt} \\
2N\text{-}H_2SO_4 & E'_0 = & 0\cdot08 \ \ ,, \\
7N\text{-}H_2SO_4 & E'_0 = & 0\cdot10 \ \ ,, \\
5N\text{-}HCl & E'_0 = & 0\cdot0 \ \ ,,
\end{array}$$

Antimony salts are reduced to metal by tin and not by copper. Antimony is not attacked by hydrochloric acid (difference from tin). Like tin it is attacked by HNO_3 with the formation of antimonic acid of low solubility.
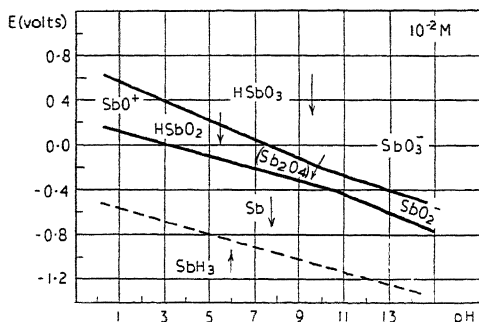
FIG. 67.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF ANTIMONY AS A FUNCTION OF pH

In alkaline solution we have

$$SbO_2^- + 2H_2O + 3e \rightleftharpoons Sb \downarrow + 4OH^- \quad . \quad -\ 0\cdot67 \text{ volt}$$

(3) $\quad 2SbO^+ + 3H_2O + 4e \rightleftharpoons Sb_2O_5\text{aq.} + 6H^+ \quad 0\cdot64$,, (calc.)
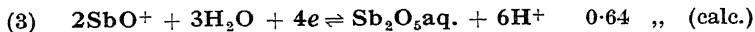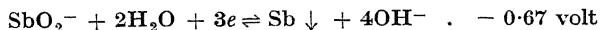
Formal potentials

In hot 3N-HCl, $E'_0 = 0\cdot7\text{–}0\cdot9$ volt.

$$SbO_3^- + H_2O + 2e \rightleftharpoons SbO_2^- + 2OH^- \quad E'_0 = -\ 0\cdot43 \text{ volt}$$
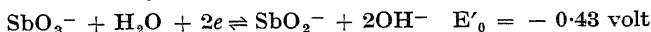
Formal potentials

$$\begin{array}{ll}
\text{In } 10N\text{-KOH} & E'_0 = -\ 0\cdot59,\ -\ 0\cdot67 \text{ volt} \\
\text{In } 5N\text{-KOH} & E'_0 = -\ 0\cdot52 \text{ volt} \\
\text{In } 3N\text{-KOH} & E'_0 = -\ 0\cdot43 \ \ ,,
\end{array}$$

The reactions are little different from those of arsenic in all solutions; this applies particularly to rates of reactions (see p. 224). SbO_2^- reduces Bi(III), As(III), Hg(II), Ag(I) to the metallic state. SbO_3^- cannot be reduced in alkaline solution.

16

Detection.—Rhodamine B (diethyl-*m*-aminophenolphthalein) gives in acid solution a violet compound with Sb(V) which can be extracted with benzene.

Solutions required.—Rhodamine solution:

Rhodamine B	0·25 g
Water	250 ml
HCl conc.	250 ml

Ceric sulphate approx. 0·1M (or 0·1-N permanganate).
10 per cent hydroxylamine hydrochloride.
Benzene.

Procedure.—To a drop of the solution to be examined in a micro-centrifuge tube, add a drop of ceric sulphate or of permanganate to oxidize Sb(III) to Sb(V) if necessary, then a drop of hydroxylamine hydrochloride in order to reduce the excess of oxidant. Add a drop of rhodamine, wait 15 seconds, add 5–6 drops of benzene. Shake.

Concentration limit.—50 p.p.m.

Interfering substances.—W(VI) and Mo(VI) give precipitates which should be centrifuged if present in large quantity. Otherwise the reaction is specific.

TIN

$$Sn = 118·7$$

States of oxidation.—II$^+$ and IV$^+$. Similar to germanium. The cations are less acid than those of antimony and arsenic. The hydroxides and sulphides give anions which are a little less stable than those of As and Sb. The redox systems are more reducing than the corresponding systems of antimony.

IV	V
Ge	As
Sn	Sb
Pb	

Sn(II)

Influence of *p*H.—Sn^{2+}, which is colourless, is present in acid solutions. The existence of SnOH$^+$, Sn$_2$(OH)$_2^{2+}$, or Sn$_2$O^{2+} has been demonstrated. The hydroxide precipitates towards *p*H 1·5 (0·01M) in the absence of complexes (perchloric acid) and redissolves towards *p*H 13·0 giving the colourless anion HSnO$_2^-$. Sn(OH)$_2$ is white, it dehydrates to black SnO. The solutions of HSnO$_2^-$ slowly precipitate black SnO. Basic salts can come down during neutralization, for example Sn(OH)Cl.

Complexes.—Chloride:—SnCl$^+$, SnCl$_3^-$, SnCl$_4^{2-}$ and perhaps SnCl$_2$. Very stable oxalate complexes. No sulphide complexes or very low stability ones.

Low-solubility compounds.—The brown sulphide SnS has a low solubility in 0·25N-HCl and redissolves in 5N-HCl. Solubility in alkali low. The polysulphides redissolve, forming sulphide complexes of Sn(IV).
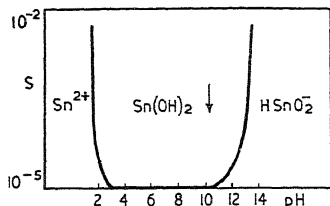
FIG. 68.—APPARENT SOLUBILITY OF Sn(II) HYDROXIDE AS A FUNCTION OF *p*H

Equilibrium constants

$$Sn(OH)_2 \downarrow \rightleftharpoons Sn^{2+} + 2OH^- \quad \ldots \ldots \ldots \quad 27$$
$$Sn(OH)_2 \downarrow \rightleftharpoons HSnO_2^- + H^+ \quad \ldots \ldots \ldots \quad 15$$
$$SnS \downarrow \rightleftharpoons Sn^{2+} + S^{2-} \quad \ldots \ldots \ldots \ldots \quad 28 \cdot 1$$
$$SnCl_4{}^{2-} \rightleftharpoons SnCl_3^- + Cl^-; \quad pk_4 = -0 \cdot 5; \; pk_3 = -0 \cdot 2;$$
$$pk_2 = 0 \cdot 7; \; pk_1 = 1 \cdot 5$$
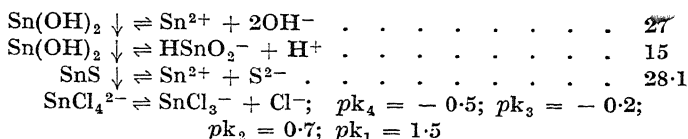
Sn(IV)

Influence of pH.—The cations exist in very acid solution. Towards pH 0·5 the white hydroxide precipitates so long as complex-forming substances are absent, i.e. in $HClO_4$ or HNO_3. It can be colloidal but in all cases it ages very rapidly and its solubility becomes very low. It redissolves with difficulty in conc. HCl or H_2SO_4 or in strong alkali; it is peptized before going into the ionized condition and it can then be reprecipitated either in the hot or on standing.

Freshly precipitated, it redissolves even at pH 9 and certainly in more acid solution. The anions $HSnO_3^-$ and $SnO_3{}^{2-}$ (or $Sn(OH)_6{}^{2-}$) are colourless.

Condensed ions are formed in acid and alkaline solution.

Complexes.—Various chloride and sulphide complexes: $SnCl_2{}^{2+}$, $SnCl_3^+$, $SnCl_4$, $SnCl_5^-$, $SnCl_6{}^{2-}$; $SnCl_4$ boils at $120°$.

There are numerous stable complexes: oxalate, tartrate, fluoride. The oxalate and fluoride complexes are not precipitated by hydrogen sulphide

FIG. 69.—APPARENT SOLUBILITY OF Sn(IV) HYDROXIDE AS A FUNCTION OF pH

(difference from Sb(III)). The fluoride complex is so stable that it cannot be reduced by Zn or Al; however, NH_3 precipitates it incompletely. Boric acid destroys the complex sufficiently for SnS_2 to be precipitated. Sulphite complexes, destroyed at pH 10–11. In conc. HCl, Sn(III) complexes exist.

Low-solubility compounds.—The yellow sulphide SnS_2 is completely precipitated in 2N-HCl and redissolved in conc. HCl. It also dissolves in ammonia whence the stannic hydroxide reprecipitates slowly. It is dissolved by S^{2-} to give sulphide complexes.

Equilibrium constants

$$Sn(OH)_4 \downarrow \quad \rightleftharpoons Sn^{4+} + OH^- \quad \ldots \ldots \ldots \quad 56$$
$$Sn(OH)_4 \downarrow \rightleftharpoons SnO_3{}^{2-} + 2H^+ + H_2O \quad \ldots \ldots \quad 32 \cdot 1$$
$$Sn \; cupferron_4 \downarrow \rightleftharpoons Sn^{4+} + 4 \; cupferron^- \quad \ldots \ldots \quad 34 \cdot 1$$

Redox

(1) $\quad$ $Sn^{2+} + 2e \rightleftharpoons Sn \downarrow \quad E_0 = -0 \cdot 14$ volt
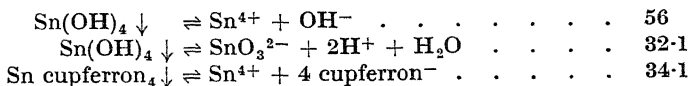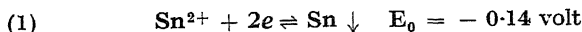
Formal potentials.— $-0 \cdot 20$ volt in N-H Cland N-H_2SO_4. Conc. HCl

attacks tin slowly. HNO_3 gives the white developed stannic hydroxide. Zn and Al precipitate tin.

$$HSnO_2^- + H_2O + 2e \rightleftharpoons Sn \downarrow + 3OH^- \quad . \quad . \quad . \quad . \quad -0.90 \text{ volt}$$

(2) $\quad\quad\quad Sn^{4+} + 2e \rightleftharpoons Sn^{2+} \quad E_0 = 0.15 \text{ volt}$
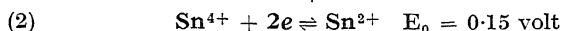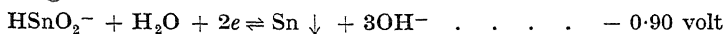
Formal potentials.—In N-HCl: 0.15 volt (approx.); in 5N-HCl 0.10 volt. In 0.1N-HCl: 0.07 volt; in 9N-H_2SO_4: 0.40 volt.

Sn(IV) is only reduced slowly, infinitely slowly in $HClO_4$, fairly slowly in H_2SO_4, more rapidly in HCl. H_2SO_3 does not reduce stannic tin. (Difference from Sb(V) and As(V).)
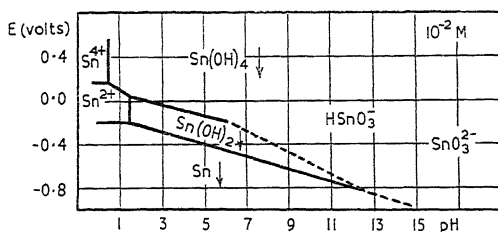
FIG. 70.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF TIN AS A FUNCTION OF *p*H

Stannous salts oxidize relatively slowly in air. Hg(II), Au(III), As(III) are reduced to the metallic state by stannous chloride in acid solution. In alkali:

$$SnO_3^{2-} + 3H^+ + 2e \rightleftharpoons HSnO_2^- + H_2O \quad . \quad -0.96 \text{ volt } (pH\ 14) \text{ (calc.)}$$
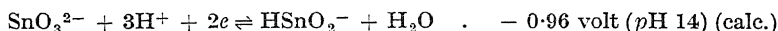
From fig. 70 it can be seen that in sufficiently alkaline solution $HSnO_2^-$ is not stable. It disproportionates (slowly) into SnO_3^{2-} and black Sn which precipitates: $2HSnO_2^- \longrightarrow Sn \downarrow + SnO_3^{2-} + H_2O$.

Stannous tin is a strong reductant in alkaline solution, it oxidizes rapidly in the air. Bi(III) is reduced to the metal.

Detection

In general the reducing power of tin in the II oxidation state is utilized. It is necessary to reduce stannic tin, which can be done in the hot with antimony or iron powders.

Iodine—iodide—starch paste.—Reaction.—Sn(IV) is first reduced to Sn(II). The reducing power of Sn(II) is then shown by the decoloration of the iodine—iodide—starch paste mixture which is blue.

Solutions required.—(1) *Iodine—iodide—starch solution.*—(*a*) N/1000 reagent: 1 ml. of 0.1N iodine solution (12.7 g iodine + 40 g KI per litre); add starch paste until a maximum blue coloration is obtained and then some millilitres in excess; dilute to 100 ml with water.

(*b*) N/4000 reagent; 1 volume of reagent (*a*) + 3 vol. water. These reagents can only be kept for a few days.

(2) *Pure iron powder.*

Procedure.—Treat 3 drops of solution with a little iron powder. Boil 1 minute. Centrifuge or leave to stand. Mix 1 drop of this solution

(1–6N-HCl) with 1 drop of reagent. In the presence of Sn there is an immediate decoloration.

Note.—In very strong HCl, iodine can be sufficiently complexed to the state of I_2Cl^- for the coloration with starch to disappear. The fact that a drop of the reagent used cannot be so decolorized is tested by simple addition of a drop of 6N-HCl. If there is a decoloration of the blank test a new solution of the reagent with freshly prepared starch paste must be made up.

Concentration limit.—Reagent (*a*) 5.10^{-4} g.-ion/litre (50 p.p.m.).

Reagent (*b*) 10^{-4} g.-ion/litre (10 p.p.m.).

If a large sensitivity is not required it is better to use reagent (*a*) which gives a much more distinct reaction, in particular when the solution to be examined contains ions which can interfere in virtue of their own colour.

Interfering ions.—The reaction used being one of redox, a certain number of reductants can interfere.

After reduction by iron in acid some metals can give rise to reducing compounds:

Cr(III): is not reduced, does not interfere.

Cu(II), Hg(II): are reduced to metal; do not interfere.

In the presence of these ions it is recommended to carry on the boiling with iron powder, because an incomplete reduction can give rise to the presence of Cu(I) or Hg(I), which would interfere.

U(VI): is reduced to U(IV) (green); in sufficiently acid solution this does not interfere because it reacts very slowly with iodine; the test should then be carried out thus: mix a drop of solution reduced by iron with a drop of 12N-HCl; add the mixture to a drop of reagent.

Ti(IV): is reduced at least partly to violet Ti(III). Same note and same procedure as for uranium.

W(VI): if the solution contains W, which interferes because on reduction it gives an intense blue colour, it should be separated by cinchonine reagent.

Cinchonine	12 g
Conc. HCl	50 ml
Water	50 ml

Procedure.—1 drop of the reagent is added to 5 drops of the solution; boil; then add iron powder and reduce as usual. The blue coloration should not appear unless the precipitation of W is incomplete. Carry out the test on this reduced solution.

Concentration limit.—10^{-3} g.-ion/litre with reagent (*a*) (100 p.p.m.).

Mo(VI), V(V) and V(IV) are reduced to Mo(III) (red), V(II) or V(III); in the presence of phosphates, Mo is reduced to molybdenum blue. In all these cases there is a slow decoloration of the reagent, and the reaction is doubtful; it is better to make a separation (and quite essential when molybdenum blue is formed, for this masks the reaction).

Reagent.—2 per cent alcoholic solution of α-benzoin oxime.

Procedure.—If V(IV) is present (blue solution) it is oxidized at the start with a crystal of persulphate, at the boil.

To 5 drops of solution, add 2 drops of reagent, and wait a few minutes. Centrifuge. Test for completion of precipitation by adding a further drop of reagent. Separate the supernatant liquid and carry out the reduction upon it.

Concentration limit.—2.10^{-3} g.-ion/litre with reagent (*a*) (200 p.p.m.).

Ions which precipitate or complex I^- sufficiently, for example Hg(II), interfere, since they decolorize the starch paste. They are separated in the course of the preceding operations.

Detection of Sn(II).—*Reduction of methylene blue.*—Sn(II) can reduce certain redox indicators, for example methylene blue in N-HCl, decolorizing them. The reaction is specific for Sn(II) in these solutions. It is used for the detection of Sn(II) in the initial solution at the start of the analysis. This preliminary detection is necessary, because Sn(II) interferes in the detection of other elements.

Solution required.—0·01 per cent solution of methylene blue in N-HCl.

Procedure.—Mix a drop of the reagent with a drop of the solution, then wait. Decoloration of the solution indicates the presence of an energetic reductant, in particular of Sn(II). Comparison may be made with a blank containing a drop of water and a drop of reagent.

Concentration limit.—3.10^{-4} g.-ion of Sn(II) per litre, at the end of 6 minutes (40 p.p.m.).

Interfering substances.—Methylene blue is a redox indicator which is reduced by a number of ions. Only those which are sufficiently stable in the air to be present in analysis are of interest to us; these are Sn(II), VO^{2+}, Fe^{2+} alone or in the presence of H_3PO_4. The reaction is then specific for Sn(II).

Coloured ions can reduce the sensitivity, e.g. Cr(III).

GERMANIUM

Ge = 72·6

Certain of its properties are indicated by its place in the periodic classification. There are three states of oxidation: IV^-, II^+, IV^+. It is intermediate between Sn and As, but nearer to Sn in practically all its properties.

III	IV	VI
Ga	Si Ge Sn	As

Ge(IV^-).—GeH_4 is a gas, decomposed into Ge and H_2 at 360°. More stable than SbH_3. Ag_4Ge is black. As with carbon, there are other germanium hydrides, e.g. Ge_2H_6, Ge_3H_8.

Ge(II)

Ge(OH)$_2$ red-orange. GeO is dark brown to black. The hydroxide is amphoteric, soluble in HCl, only slightly soluble in NH_3. GeO_2^{2-} is cherry red, very easily oxidized in the air.

GeS, deep reddish orange, is soluble in conc. HCl, and in ammonium sulphide. The anions are less stable than those of As(III), but more stable than those of Sn(II).

$GeCl_3^-$; tartrate complex which is precipitated neither by NH_3 nor by H_2S.

Ge(IV)

More acid than Sn(IV), the cations do not exist. The hydroxide is fairly soluble, 0·05M. It ages rapidly. Its solubility in HNO_3 and H_2SO_4 is low. In HCl, a complex is formed which is not precipitated until the pH is above 6. The hydroxide redissolves from pH 7·8. It can behave as an acid, H_2GeO_3, and also forms condensed ions, $H_2Ge_5O_{11}$, $pk_2 = \sim 9; pk_1 = 13$.

White GeS_2 is of low solubility in 3N-HCl. It only precipitates in very acid solution, but is slightly soluble in water, soluble in NH_3.

$GeCl_4$ is a liquid boiling at 85–86°.

Complexes.—With Cl^-; with polyalcohols. Very stable oxalate and fluoride complexes which are not precipitated by H_2S.

Sulphide complexes such as $Ge_2S_5{}^{2-}$ very stable, colourless, destroyed in 6N-HCl. GeO_2 is soluble in the presence of H_2S giving complexes with S^{2-}.

The germanates, including the alkaline earth ones, are in general of low solubility.

Equilibrium constants

$$H_2Ge_5O_{11} \downarrow \rightleftharpoons HGe_5O_{11}{}^- + H^+ \quad . \quad . \quad . \quad 10$$
$$H_2Ge_5O_{11} \rightleftharpoons HGe_5O_{11}{}^- + H^+ \quad . \quad . \quad . \quad 8 \cdot 6\text{–}9$$
$$HGe_5O_{11}{}^- \rightleftharpoons Ge_5O_{11}{}^{2-} + H^+ \quad . \quad . \quad . \quad 12 \cdot 7\text{–}13$$
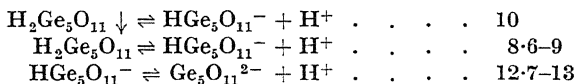
Redox

(1) GeH_4 is formed by reduction with zinc or sodium amalgam.

(2) $\quad GeO_2$ (dissolved) $+ H^+ + 4e \rightleftharpoons Ge \downarrow + 2H_2O$

In N-$HClO_4$ (saturated with oxide) (0·05M), E = 0·13 volt.

$GeO_2 \downarrow$ (developed) $+ 4H^+ + 4e \rightleftharpoons Ge \downarrow + 2H_2O \quad E_0 = 0 \cdot 02$ volt
Germanium displaces Hg, but not Cu.

(3) GeO_2/Ge^{2+}.

Hypophosphorous acid reduces Ge(IV) to Ge(II). Ge^{2+} is a reductant which oxidizes in the air.

In alkaline solution:

$$HGeO_3{}^- + 2H^+ + 2e \rightleftharpoons HGeO_2{}^- + H_2O; \sim - 1 \cdot 4 \text{ volts}$$

at pH 14 (calculated): $HGeO_4{}^-$ disproportionates into $HGeO_3{}^-$ and Ge.

Reagents.—Germanium is in general detected in traces, either spectroscopically or by the formation of a germanomolybdic complex analogous to the silicomolybdic complex, or else by its action in conc. H_2SO_4 on quinalizarin, an action which is analogous to that of boric acid (p. 321).

II. VANADIUM—MOLYBDENUM—TUNGSTEN

Va	VIa
V	Cr
Nb	Mo
Ta	W

Elements of an '*a*' group of the periodic table whose sulphides have a low solubility. Sulphide complexes are formed as in the preceding group.

VANADIUM

V = 50·95

States of oxidation.—All from II+ to V+. In II+ vanadium resembles the zinc group: in III+ its properties are similar to those of Fe(III), Al(III), Ti(III). In the IV+ state we have the vanadyl salts,

VO^{2+} stable in the air, which put vanadium in this state in the ammonia group. Vanadium has the oxidation number V in the vanadates which resemble the phosphates and arsenates and also $Mo(VI)$, $W(VI)$, and $Cr(VI)$.
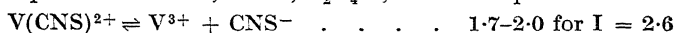
V(II).—Violet cations. Not stable in air.

V(III).—Vanadous salts. V^{3+}, VOH^{2+}, green. $V(OH)_3$ precipitates around pH 4–5. Oxidizes in the air.

Complexes with CN^-, CNS^-, $C_2O_4^{2-}$, stable complexes with F^-.

$$V(CNS)^{2+} \rightleftharpoons V^{3+} + CNS^- \quad . \quad . \quad . \quad . \quad 1 \cdot 7\text{--}2 \cdot 0 \text{ for } I = 2 \cdot 6$$

V(IV)

Vanadyl salts. VO^{2+} is blue, and stable in air in acid solution. $VO(OH)_2$ is greyish brown and precipitates at pH $4 \cdot 1$ ($0 \cdot 01$M). It develops rapidly, and redissolves very slowly in alkaline solution giving $HV_2O_5^-$ or $V_4O_9^{2-}$, reddish brown, then red. The hydroxide is precipitated by acidifying the alkaline solution to pH $8 \cdot 25$ ($0 \cdot 01$M).
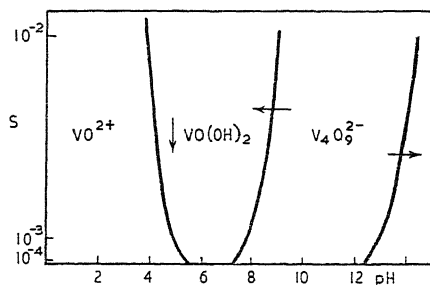
FIG. 71.—APPARENT SOLUBILITY OF V(IV) HYDROXIDE
AS A FUNCTION OF pH

Complexes.—Low-stability fluoride and very low stability thiocyanate complexes are known. Fairly stable oxalate and very stable tartrate complexes are formed.

Equilibrium constants

$$
\begin{array}{llr}
VO(OH)_2 \downarrow \rightleftharpoons VO^{2+} + 2OH^- & . \quad . \quad . \quad . \quad . & 22 \cdot 1 \\
VO^{2+} + H_2O \rightleftharpoons VOOH^+ + H^+ & . \quad . \quad . \quad . \quad . & 4 \cdot 8 \\
2VO(OH)_2 \downarrow \rightleftharpoons V_2O_5H^- + H^+ + H_2O & . \quad . \quad . \quad . & 10 \cdot 5 \\
VO(C_2O_4)_2^{2-} \rightleftharpoons VO^{2+} + 2C_2O_4^{2-} & . \quad . \quad . \quad . & 12 \cdot 0 \\
VO(OH)C_2O_4^- \rightleftharpoons VOOH^+ + C_2O_4^{2-} & . \quad . \quad . \quad . & 6 \cdot 5 \\
VO \text{ tart.} \rightleftharpoons VO \text{ tart.}^- + H^+ & . \quad . \quad . \quad . & 2 \cdot 8 \\
VO \text{ tart.}^- \rightleftharpoons VO \text{ tart.}^{2-} + H^+ & . \quad . \quad . \quad . & 6 \cdot 8 \\
VOF^+ \rightleftharpoons VO^{2+} + F^- & . \quad . \quad . \quad . \quad . & 3 \cdot 2 \\
VO(CNS)^+ \rightleftharpoons VO^{2+} + CNS^- & . \quad . \quad . \quad . & 0 \cdot 9 \, (I = 2 \cdot 6)
\end{array}
$$

V(V)

In the oxidation state V, vanadium is placed in the periodic table below $P(V)$ and alongside $Cr(VI)$. It resembles both elements.

Influence of pH.—In strong acid, light yellow VO_2^+ is formed.

Reddish-brown V_2O_5,aq. is fairly soluble: 0·07M (0·02M in the hot at pH 2). It develops rapidly and its solubility falls. Its minimum solubility is at pH 1·6. It then transforms into $H_3V_2O_7^-$, orange. This transforms into $H_3V_2O_7^{2-}$ when the solution is made very alkaline with NaOH.

If the solution is alkaline at the start, the phenomena are different; first we have HVO_4^{2-}, colourless—the orthovanadate ion. The rapid addition of acid in the cold causes orange ions to be formed which only transform very slowly, faster in the hot, into the metavanadate ion $H_2VO_4^-$ (or VO_3^-) which is colourless. This happens at pH 9·4. In more acid solution, pH 6·5,

$$2H_2VO_4^- + H^+ \longrightarrow H_3V_2O_7^- \text{ (orange)} + H_2O$$

The reverse reaction is very slow.

Note.—These ions are possibly more condensed than is indicated, e.g. $HV_6O_{17}^{3-}$.

Low-solubility compounds.—The majority of the vanadates other than those of the alkali metals are of low solubility. The solubility of NH_4VO_3 is fairly low in the presence of an excess of NH_4^+ ions. The vanadates of lead and mercury have very low solubilities (analogy with Mo(VI), W(VI), Cr(VI)). The brown sulphide V_2S_5 has a low solubility in very dilute acid. It redissolves in alkali and in sulphides giving orange-red sulphide complexes. H_2S does not precipitate them from acid solutions of V(V) which is then reduced to V(IV).
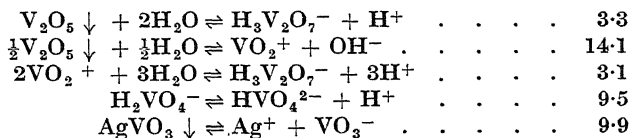

FIG. 72.—APPARENT SOLUBILITY OF V(V) HYDROXIDE AS A FUNCTION OF pH

Complexes.—Phosphovanadate, phosphovanadotungstate ones are known, they are yellow and soluble in organic solvents.

With hydrogen peroxide, stable orange compounds are formed which are stable even in strong acid.

Equilibrium constants

$$V_2O_5 \downarrow + 2H_2O \rightleftharpoons H_3V_2O_7^- + H^+ \quad . \quad . \quad . \quad 3\cdot3$$
$$\tfrac{1}{2}V_2O_5 \downarrow + \tfrac{1}{2}H_2O \rightleftharpoons VO_2^+ + OH^- \quad . \quad . \quad . \quad . \quad 14\cdot1$$
$$2VO_2^+ + 3H_2O \rightleftharpoons H_3V_2O_7^- + 3H^+ \quad . \quad . \quad . \quad 3\cdot1$$
$$H_2VO_4^- \rightleftharpoons HVO_4^{2-} + H^+ \quad . \quad . \quad . \quad 9\cdot5$$
$$AgVO_3 \downarrow \rightleftharpoons Ag^+ + VO_3^- \quad . \quad . \quad . \quad . \quad 9\cdot9$$

Redox

(1) $$VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O$$
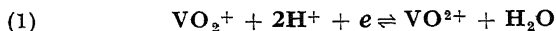
$$E = 1\cdot01 + 0\cdot06 \log \frac{|VO_2^+| \cdot |H^+|^2}{|VO^{2+}|} \text{ volts}$$

Same potential in HCl and H_2SO_4. In 9N-$HClO_4$ and 8N-H_2SO_4, $E'_0 = 1\cdot30$.

In alkali, the potential becomes very reducing: $E'_0 = -0\cdot74$ at pH 14.

The system V(V)/V(IV) has properties similar to those of the system Cr(VI)/Cr(III). The oxidation of vanadyl salts, slow in very acid solution, is still fairly slow at pH 1·5. It is speeded up by heating. In neutral or

alkaline solution, the system becomes more reducing and the oxidation is very rapid, even in the air.

FIG. 73.—FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS
OF VANADIUM AS A FUNCTION OF pH

V(V) acts as a rather slow oxidant in solution. SO_2, H_2S, Fe^{2+}, alcohol, etc., reduce it. In weak acid solution, the rate of the reaction falls to zero.

(2) $VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+}$ $E_0 = 0.34$ volt
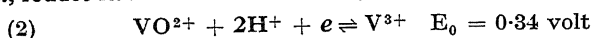
The formal potential is 0·34 volt in N-H_2SO_4. V^{3+} (perhaps VOH^{2+}) oxidizes in the air to give VO^{2+} which is stable in acid solution. In weak acid, neutral, or alkaline solution, the oxidation is more rapid and V(V) is obtained.
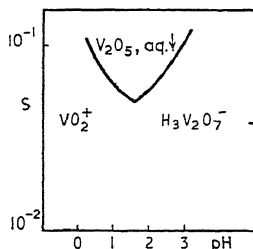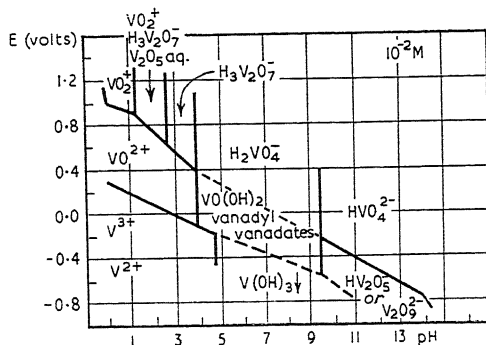
(3) $V^{3+} + e \rightleftharpoons V^{2+}$ $E_0 = -0.21$ to -0.25 volt
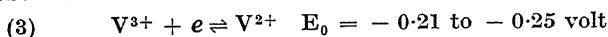
Salts of V(II) are obtained by reduction with zinc or zinc amalgam in very acid solution.

They are very strong reductants: in acid solution, NO_3^- gives NH_4^+, ClO_3^- and ClO_4^- give Cl^-, Cu^{2+} goes to Cu, H^+ is reduced slowly to H_2. They oxidize in the air. In alkalis, the reducing power is even stronger. $V(OH)_2$ reacts with water with liberation of hydrogen.

(4) *Metal*

$V^{2+} + 2e \rightleftharpoons V \downarrow$ . . . . . -1.5 ± 0.3 volt (calc.)
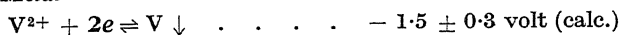
Vanadium is not attacked by water, air, or dilute acids; it is passive. It is attacked by oxidants: chlorine, nitric acid, and also by hydrofluoric acid on account of the formation of a complex.

Detection

Hydrogen peroxide.—*Reactions.*—V(IV) and V(V) in acid solution give a reddish-orange coloration.

Materials required

Hydrogen peroxide, 5 vol.

Solid NaF.

Procedure.—To a drop of the solution, add a drop of 4N-HCl, and a drop of hydrogen peroxide. The absence of a coloration indicates the absence of vanadium or titanium.

Limit of sensitivity.—10^{-3} g.-ion/litre (50 p.p.m.).

Interfering substances.—A large number of ions give similar colorations. The majority of these are rather pale and do not interfere greatly: U(VI), Mo(VI), W(VI), etc.

The addition of fluoride which forms complexes strongly with Ti(IV) and Fe(III) causes the colours due to these ions to disappear. That due to vanadium weakens slightly, the sensitivity is reduced to 10^{-2} g.-ion/litre.

MOLYBDENUM—TUNGSTEN

$$Mo = 96 \cdot 0; \quad W = 184 \cdot 0$$

States of oxidation.—The more important are III, V, and VI. Compounds in the latter state are stable in air, thus being similar to those of W(VI) and Cr(VI).
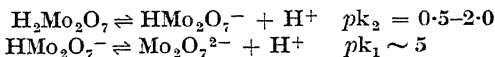
Mo(VI)

The cations do not exist except in very acid solution: MoO_2^{2+}. The hydroxides and the anions are often condensed, and the equilibria with the condensed ions are often attained only very slowly. They also depend naturally on the concentrations.

The stable hydroxide is $H_2Mo_2O_7$; H_2MoO_4 transforms slowly into $H_2Mo_2O_7$ by dehydration.

$$H_2Mo_2O_7 \rightleftharpoons HMo_2O_7^- + H^+ \qquad pk_2 = 0 \cdot 5\text{-}2 \cdot 0$$
$$HMo_2O_7^- \rightleftharpoons Mo_2O_7^{2-} + H^+ \qquad pk_1 \sim 5$$

$Mo_2O_7^{2-}$ hydrates slowly:

$$Mo_2O_7^{2-} + H_2O \rightleftharpoons 2HMoO_4^-$$
$$HMoO_4^- \rightleftharpoons MoO_4^{2-} + H^+; \quad pK \sim 6$$
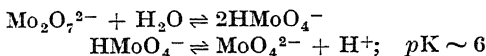
Ions more condensed such as $Mo_4O_{13}^{2-}$ ($2HMo_2O_7^-$. H_2O) exist.

White H_2MoO_4 is soluble in strong acid and in alkali as weak as ammonia. MoO_3.$2H_2O$, yellow, has a low solubility in acid solution, but is soluble in alkali. When ammonium molybdate is acidified a precipitate is thrown down which does not redissolve in HNO_3.

White MoO_3 is volatile above 550°.

W(VI)

Tungstic acid is yellowish white. It dehydrates in the hot giving yellow WO_3, not very soluble in strong acids, volatile at about 900°. WO_3 is often colloidal, and should be washed with strong acids or salts. It does not flocculate completely except when evaporated to dryness in strong acids. It is soluble in ammonia giving tungstates. Tungstates, like molybdates and vanadates, have very variable formulae, depending on the concentration and the *p*H of the solution.

Complexes.—Mo(VI) and W(VI).—Complexes with chloride, phosphate, arsenate and vanadate ions, and with fluoride, citrate, tartrate, and oxalate ions, all of which inhibit the precipitation of the hydroxide to some extent. Ammonium phosphomolybdate $(NH_4)_3(PO_4)$.$12MoO_3$, yellow, slightly soluble in nitric acid, soluble in alkalis, soluble in organic solvents. Some complexes with W(VI), analogous ones with Si(IV).

Action of hydrogen sulphide.—Mo(VI).—In acid solution, a blue coloration is produced as a result of partial reduction and precipitation of MoS_3 which is brown to black; the precipitation is not quantitative. MoS_3 has a low solubility in dilute HCl, but is soluble in ammonium sulphide giving a yellow to orange coloration (analogous to V(V), W(VI)). The sulphide complex is destroyed at pH 6–7 (0·01M).

W(VI).—WS_3 is not precipitated by H_2S. But ammonium sulphide gives the orange-yellow thio-salt, and brown WS_3 precipitates then on acidification. The sulphide complex is not destroyed completely until below pH 4.
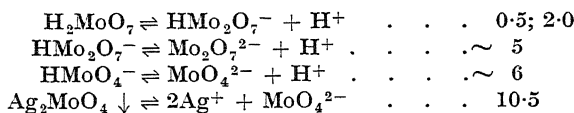
Solubility of molybdates and tungstates.—Only the alkali salts are soluble. Hg_2MoO_4, $PbMoO_4$, and the corresponding tungstates are of particularly low solubility. The ferrocyanide ion gives with molybdenum a reddish-brown precipitate whose solubility in conc. HCl is low, but which is soluble in ammonia.

A large number of tungstates of organic bases—cinchonine, rhodamine, etc.—have a low solubility in strong acids.

α-benzoin oxime gives low-solubility compounds in strong acid with Mo(VI) and with W(VI).

Equilibrium constants

Mo(VI)

$$H_2MoO_7 \rightleftharpoons HMo_2O_7^- + H^+ \quad . \quad . \quad . \quad 0·5; \ 2·0$$
$$HMo_2O_7^- \rightleftharpoons Mo_2O_7^{2-} + H^+ . \quad . \quad . \sim 5$$
$$HMoO_4^- \rightleftharpoons MoO_4^{2-} + H^+ \quad . \quad . \quad . \sim 6$$
$$Ag_2MoO_4 \downarrow \rightleftharpoons 2Ag^+ + MoO_4^{2-} \quad . \quad . \quad . \quad 10·5$$

W(VI)

$$\left.\begin{array}{l} H_3WO_5^- \rightleftharpoons H_2WO_5^{2-} + H^+ \\ H_2WO_5^{2-} \rightleftharpoons HWO_5^{3-} + H^+ \\ HWO_5^{3-} \rightleftharpoons WO_5^{4-} + H^+ \end{array}\right\} \quad . \quad . \quad . \quad . \quad 6\text{–}8$$
$$Ag_2WO_4 \downarrow \rightleftharpoons 2Ag^+ + WO_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad 9·3$$
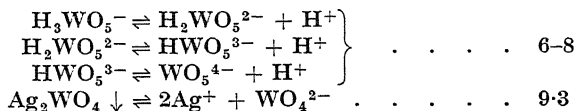
Other states of oxidation.—The principal ones are (V) and (III).

Mo(V).—In 8N-HCl, Mo(V) gives $MoOCl_5^{2-}$, purplish green, and in 2N-HCl, yellowish-brown to deep-brown $MoO_3^+.MoO(OH)_3$.

$Mo(CNS)_5$, crimson, soluble in organic solvents; $Mo(CN)_3^{3-}$ very stable.

In HCl solutions weaker than 2N, deep blue precipitates or colloidal solutions of $Mo_2O_5.xMoO_3$ are obtained easily. Blue complexes such as $H_3PO_4(MoO_2.4MoO_3)_2$ are known.

W(V).—W_2O_5 is blue. $W(CN)_8^{3-}$ is very stable.

Mo(IV) exists in $Mo(CN)_8^{4-}$, a very stable complex in which Mo is stabilized in the IV oxidation state.

W(IV).—Brown; fluoride complexes are stable in the air; oxalate complexes are known.

Mo(III).—In 9N-HCl, brick-red $MoCl_6^{3-}$ and $MoCl_5^{2-}$ are stable in air. In 2·5–4N-HCl, the deep olive Mo^{3+} exists. It is oxidizable and on the other hand transforms itself slowly into a red compound. Brownish-black $Mo(OH)_3$ is precipitated by NH_3.

Complexes with $C_2O_4^{2-}$, CNS^-, etc. $Mo(CNS)_6^{3-}$ is yellow.

W(III).—Red unstable $WCl_5{}^{2-}$, a strong reductant, transforms itself into $W_2Cl_9{}^{3-}$ which is yellow to yellowish green.

Mo(II) and W(II).—Not stable in solution.

Redox

Mo(VI) and Mo(V).—Reduction involves initially the formation of blue compounds whose oxidation number is intermediate between V and VI, particularly in weak HCl.
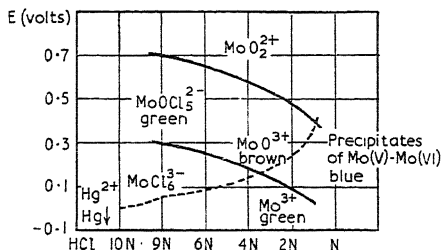
FIG. 74.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE SYSTEMS Mo(VI)/Mo(V)/Mo(III) AND Hg(II)/Hg IN HCl

In HCl, the formal potentials are shown in fig. 74. In fairly conc. HCl, Mo(VI) is reduced to green $MoOCl_5{}^{2-}$, and in dilute HCl to brown MoO^{3+}.

In alkali Mo(VI) is only reduced infinitely slowly.

In H_2SO_4 the properties are little different. Mo(V) is stable in the air in 4N-HCl.

H_2S reduces it to molybdenum blue. In HCl, Ag and Hg reduce it to (V) and (III) according to the concentration of the HCl (fig. 74).

Mo(V)/Mo(III).—$MoO^{3+} + 2H^+ + 2e \rightleftharpoons Mo^{3+} + H_2O$

With green Mo(III), $E'_0 = 0.11$ volt in 2N-HCl.

With red Mo(III), $MoCl_6{}^{3-}$, $E'_0 = 0.26$ volt in 8N-HCl (see fig. 74).

Green Mo(III) oxidizes in the air, but the red modification does so much more slowly.

Zinc in dilute acid reduces Mo(VI) to Mo(III).

Mo.—Molybdenum easily becomes passive. It is little attacked by conc. HCl, but is dissolved by conc. HNO_3 and by hot conc. H_2SO_4. It can be attacked by an oxidizing alkaline fusion.

W(VI)/W(V)

$WO_2{}^{2+} + 2H^+ + e \rightleftharpoons WO^{3+} + H_2O$ E = 0.27 volt in conc. HCl
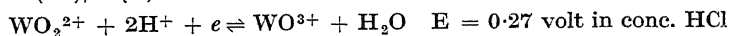
Stannous chloride precipitates blue W_2O_5.

W(VI)/W(III).—In conc. HCl, $W_2Cl_9{}^{3-}$ is formed. $E'_0 = 0.0$ volt.

W(V)/W(III).—$E'_0 = -0.30$ volt.

W.—The metal is passive. HCl does not attack it, conc. H_2SO_4 and hot conc. HNO_3 attack it fairly little if the metal is compact.

H_3PO_4, hot and concentrated, attacks the metal forming a complex; HF the same. Molten alkalis attack the metal, particularly when they are oxidizing.

Detection of Mo(VI)

Stannous chloride and thiocyanate.—*Reaction.*—A solution of molybdate in hydrochloric acid carefully reduced with stannous ions gives a red complex with thiocyanate ions which gives a red solution in benzyl alcohol.

Solutions required.—5 per cent stannous chloride in 2·5N-HCl. Add some particles of tin to the solution.

Saturated ammonium thiocyanate solution.

Benzyl alcohol.

Procedure.—The solution should be strongly acid with HCl. If it does not contain any Fe^{3+}, to a drop of it add a drop of stannous chloride, a drop of the thiocyanate, and shake. A red coloration forms, soluble in benzyl alcohol giving a violet-red solution, the reaction being then very sensitive.

Concentration limit.—10^{-4}–5.10^{-5} of Mo(VI) per litre (5–10 p.p.m.)

Interfering substances.—A certain number of ions give colorations (see ferric iron, p. 165). The excess of stannous chloride causes the colorations due to Fe^{3+} and Cu^{2+} to disappear.

In the presence of Co^{2+}, the colour due to this ion superimposes itself on that due to molybdenum, particularly when using benzyl alcohol. Much Co^{2+} interferes. In that case the procedure should be: put a drop of solution in a centrifuge tube. Add a drop of 4N-NaOH and a drop of 5 vol. H_2O_2. Shake. Centrifuge. Pipette a drop of the supernatant solution on to a spot plate. Re-acidify with a drop of 4N-HCl, and repeat the test.

V(IV) and V(V) decrease the sensitivity.

Se(IV), Te(IV), and Te(VI) give precipitates of Se and Te.

W(VI) gives a blue precipitate of W_2O_5, not soluble in benzyl alcohol. See page 166 for notes about reactions with CNS^-.

Precipitation by α-benzoin oxime.—In very dilute acid, some ions only precipitate.

Solutions required.—2 per cent alcoholic α-benzoin oxime. 4N-HCl.

Procedure.—In a centrifuge tube, add a drop of acid to a drop of solution, then a drop of reagent. Wait 30 seconds.

Concentration limit and selectivity.—The following precipitate: Mo(VI) 5.10^{-4}; W(VI) 5.10^{-4}; V(V) 10^{-2}.

If there is no precipitate, it is unnecessary to look for W(VI) and Mo(VI).

Detection of W(VI)

Tungsten is not generally met with in acid solution; the tungstates precipitate as tungstic acid when acidified. But in the presence of phosphates, tungsten is kept in solution as a complex.

Procedure with stannous chloride.—*Reaction.*—Tungstates in conc. HCl are reduced by stannous chloride yielding a deep blue precipitate of the blue oxide of tungsten, W_2O_5, which persists if an excess of stannous chloride is introduced (whereas under the same conditions, molybdates give a blue coloration which disappears when excess is added).

Solution required.—Solid stannous chloride. Conc. HCl.

Procedure.—Place a drop of solution on a spot plate, add a drop of acid and a crystal of solid stannous chloride.

Concentration limit.—3.10^{-3} g.-ion of W(VI) per litre (500 p.p.m.).

Interfering ions.—The precious metals give black precipitates, and mercury as well. As precipitates slowly. Se(IV), Te(IV), Te(VI) precipitate the corresponding elements.

Mercury is disposed of thus: to 1 drop of solution, add 3 drops of 4N-NaOH. Centrifuge. Remove 1 drop of the supernatant, and make the previous test. If the centrifuging does not bring the precipitate down very fast, warm the solution for a minute beforehand on the water bath.

CHAPTER VII

ELEMENTS HAVING LOW-SOLUBILITY CHLORIDES.

SILVER. THALLIUM

SILVER

$$Ag = 107 \cdot 9$$

States of oxidation.—The most important is I. II also occurs. III is known in the solid state, and perhaps also IV.

Ag(I)

In the periodic classification, Ag(I) is located between Cu(I) and Au(I). It resembles them in the low acidity of its cation, the hydroxide, in its low-solubility compounds and its complexes. It also resembles Tl(I).

Ib
Cu(I)
Ag(I)
Au(I)

Influence of pH.—Ag^+ is colourless. White AgOH precipitates at around pH 8 (0·01M) and dehydrates spontaneously into the brown Ag_2O.

Complexes.—Numerous. The hydroxide does not precipitate in the presence of NH_3 since ammine complexes are formed. Explosive Ag_3N and $AgNH_2$ precipitate slowly in ammoniacal solution.

The sulphite complexes decompose slowly with precipitation of silver
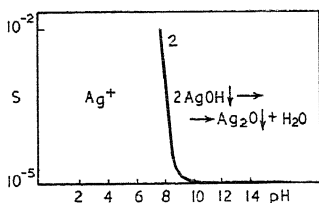
FIG. 75.—APPARENT SOLUBILITY OF SILVER HYDROXIDE AS A FUNCTION OF pH

Some complexes are very stable, such as the thiosulphate and cyanide ones.

The thiosulphate complex blackens slowly in the cold, and rapidly in the hot, particularly in acid solution, as a result of the precipitation of black Ag_2S.

Low-solubility compounds.—The solubility of nearly all silver salts is low, the only exceptions being the nitrate, perchlorate, fluoride, acetate, and chlorate.

Black Ag_2S, of very low solubility, is oxidized by hot HNO_3. $Ag[Ag(CN)_2]$ is the salt of a strong acid.

A certain number of the low-solubility compounds are coloured. Yellow: phosphate, arsenite; pale yellow: iodide; brown or brick red: dichromate, chromate, arsenate; orange: ferricyanide. The sulphide is black. The other salts are white or sometimes yellowish.

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Equilibrium constants

$$Ag_3AsO_4 \downarrow \rightleftharpoons 3Ag^+ + AsO_4^{3-} \quad \ldots \quad 22\cdot0$$

$$AgNO_2 \downarrow \rightleftharpoons Ag^+ + NO_2^- \quad \ldots \quad 3\cdot6$$

$$Ag(NO_2)_2^- \rightleftharpoons AgNO_2 \downarrow + NO_2^- \quad \ldots \quad -0\cdot8$$

$$AgN_3 \downarrow \rightleftharpoons Ag^+ + N_3^- \quad \ldots \quad 8\cdot6$$

$$Ag(NH_3)_2^+ \rightleftharpoons AgNH_3^+ + NH_3; \quad pk_2 = 3\cdot8; \; pk_1 = 3\cdot2$$
$$\text{(for I = 1 at 30°)}$$

$$AgBr \downarrow \rightleftharpoons Ag^+ + Br^- \quad \ldots \quad 12\cdot3$$

$$AgBrO_3 \downarrow \rightleftharpoons Ag^+ + BrO_3^- \quad \ldots \quad 4\cdot3$$

$$Ag(CH_3CO_2)_2^- \rightleftharpoons AgCH_3CO_2 + CH_3CO_2^-; \quad pk_2 = -0\cdot1;$$
$$pk_1 = 0\cdot7$$

$$AgCH_3CO_2 \downarrow \rightleftharpoons Ag^+ + CH_3CO_2^- \quad \ldots \quad 2\cdot7$$

$$Ag_2CO_3 \downarrow \rightleftharpoons 2Ag^+ + CO_3^{2-} \quad \ldots \quad 11\cdot1$$

$$Ag(CN)_4^{3-} \rightleftharpoons Ag(CN)_3^{2-} + CN^-; \quad pk_4 = 0; \; pk_3 = 1;$$
$$pk_2 + pk_1 = 20\cdot9$$

$$Ag[Ag(CN)_2] \downarrow \rightleftharpoons Ag^+ + Ag(CN)_2^- \quad \ldots \quad 11\cdot4$$

$$Ag_2C_2O_4 \downarrow \rightleftharpoons 2Ag^+ + C_2O_4^{2-} \quad \ldots \quad 11\cdot0$$

$$AgCNO \downarrow \rightleftharpoons Ag^+ + CNO^- \quad \ldots \quad 6\cdot6$$

$$AgCl_4^{3-} \rightleftharpoons AgCl_3^{2-} + Cl^-; \quad pk_4 + pk_3 = 0\cdot6;$$
$$pk_2 = -4\cdot3; \; AgCl \downarrow; \; pk_1 = 9\cdot7$$

$$Ag_2CrO_4 \downarrow \rightleftharpoons 2Ag^+ + CrO_4^{2-} \quad \ldots \quad 11\cdot4$$

$$Ag_2Cr_2O_7 \downarrow \rightleftharpoons 2Ag^+ + Cr_2O_7^{2-} \quad \ldots \quad 6\cdot7$$

$$Ag_2[Fe(CN)_5NO] \downarrow \rightleftharpoons 2Ag^+ + Fe(CN)_5NO^{2-} \quad \ldots \quad 12\cdot1$$

$$Ag_4[Fe(CN)_6] \downarrow \rightleftharpoons 4Ag^+ + Fe(CN)_6^{4-} \quad \ldots \quad 40\cdot8$$

$$Ag_2I_6^{4-} \rightleftharpoons Ag_2I_4^{2-} + 2I^- \quad \ldots \quad -12\cdot3$$

$$Ag_2I_4^{2-} \rightleftharpoons AgI_4^{3-} + Ag^+ \quad \ldots \quad 12\cdot9$$

$$AgI_4^{3-} \rightleftharpoons AgI \downarrow + 3I^- \quad \ldots \quad -1\cdot6$$

$$AgI \downarrow \rightleftharpoons Ag^+ + I^- \quad \ldots \quad 16\cdot05$$

$$AgIO_3 \downarrow \rightleftharpoons Ag^+ + IO_3^- \quad \ldots \quad 7\cdot3$$

$$Ag_2MoO_4 \downarrow \rightleftharpoons 2Ag^+ + MoO_4^{2-} \quad \ldots \quad 10\cdot5$$

$$\tfrac{1}{2}Ag_2O \downarrow + \tfrac{1}{2}H_2O \rightleftharpoons Ag^+ + OH^- \quad \ldots \quad 7\cdot7; \; 8\cdot0; \; 7\cdot5$$

$$\tfrac{1}{2}Ag_2O \downarrow + \tfrac{1}{2}H_2O \rightleftharpoons AgO^- + H^+ \quad \ldots \quad 17\cdot7$$

$$Ag^+ + H_2O \rightleftharpoons AgOH + H^+ \quad \ldots \quad 11\cdot7$$

$$AgOH \rightleftharpoons AgO^- + H^+ \quad \ldots \quad 12\cdot1$$

$$Ag_3PO_4 \downarrow \rightleftharpoons 3Ag^+ + PO_4^{3-} \quad \ldots \quad 20\cdot8$$

$$Ag_2SO_4 \downarrow \rightleftharpoons 2Ag^+ + SO_4^{2-} \quad \ldots \quad 4\cdot2$$

$$Ag_2S \downarrow \rightleftharpoons 2Ag^+ + S^{2-} \quad \ldots \quad 48\cdot8; \; 51\cdot2; \; 48\cdot1;$$
$$51\cdot8 \; (I = 0)$$

$$AgSH \rightleftharpoons AgS^- + H^+ \quad \ldots \quad 5\cdot3$$

$$AgSH + H^+ \rightleftharpoons Ag^+ + H_2S \quad \ldots \quad 9\cdot25$$

$$Ag(CNS)_4^{3-} \rightleftharpoons Ag(CNS)_3^{2-} + CNS^-; \quad pk_4 + pk_3 = 2\cdot4;$$
$$pk_2 = -3\cdot5; \; AgCNS \downarrow; \; pk_1 = 12\cdot0; \; 11\cdot2$$

$$Ag(SO_3)_2^{3-} \rightleftharpoons Ag^+ + 2SO_3^{2-} \quad \ldots \quad 4\cdot3; \; 8\cdot5$$

$$Ag(S_2O_3)_3^{5-} \rightleftharpoons Ag(S_2O_3)_2^{3-} + S_2O_3^{2-}; \quad pk_3 = -0\cdot5\text{-}+0\cdot5;$$
$$pk_2 = 0\text{-}0\cdot4; \; pk_1 = 13\cdot0$$

$$AgCNSe \downarrow \rightleftharpoons Ag^+ + CNSe^- \quad \ldots \quad 15\cdot4$$

$$Ag_2WO_4 \downarrow \rightleftharpoons 2Ag^+ + WO_4^{2-} \quad \ldots \quad 9\cdot3$$

$$AgVO_3 \downarrow \rightleftharpoons Ag^+ + VO_3^- \quad \ldots \quad 9\cdot9$$

$$Ag \downarrow p\text{-dimethylaminobenzylidene rhodanine} \rightleftharpoons Ag^+ + \text{rhodanine}^- \; 18\cdot1;$$
$$20\% \text{ alcohol}$$

Ag(II)

Very acid cation, which exists only in the form of complexes, e.g. with NO_3^-. The solutions are brown or black; AgO precipitates around pH 1. The nitrate complex gives a salt of Ag^+ of low solubility.

Redox.—(1) $Ag^+ + e \rightleftharpoons Ag \downarrow$ $E_0 = 0.80$ volt

This system is a little more oxidizing than that of the ferric salts. The metal can still be attacked by oxidizing acids, hot conc. HNO_3 and H_2SO_4 or by HCl in the presence of an oxidant. It is much more reducing in HCl on account of the formation of low-solubility AgCl (see p. 98).
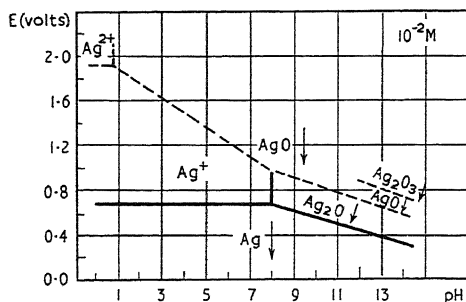
FIG. 76.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF SILVER

In the air, silver dissolves appreciably in cyanides forming the very stable complex $Ag(CN)_2^-$. In the presence of air, hydrogen sulphide converts silver into the very low solubility black Ag_2S.

$$4Ag \downarrow + 2H_2S \uparrow + O_2 \uparrow \longrightarrow 2H_2O + 2Ag_2S \downarrow$$
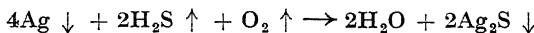
Silver salts are easily reduced, for example by Sn(II) in ammonia (just like Hg(II) and Bi(III)).

(2) $Ag^{2+} + e \rightleftharpoons Ag$ $E_0 = 1.98$ volts

Formal potentials

In 1–4N-HNO$_3$ at 0° . . . : .	1·91 volts
In 4N-HClO$_4$ at 25°	2·00 ,,
In N-NaOH	0·59 ,,

Salts of Ag(II) are unstable, because they are too oxidizing. They slowly oxidize water. Ag(II) oxidizes Mn^{2+} to MnO_4^- in the cold, Pb^{2+} to PbO_2, Ce^{3+} to Ce^{4+}.

$S_2O_8^{2-}$ oxidizes Ag^+ to Ag^{2+}.

The redox systems of silver are frequently catalytic.

(3) $Ag_2O_3 \downarrow + H_2O + 2e = 2AgO \downarrow + 2OH^-$ $E'_0 = 0.76$ volt

Detection

Precipitation of silver chloride.—It is precipitated at the start of analysis and is redissolved in ammonia, whence it is reprecipitated by an acid.

Only 10^{-4} g.-ion of Ag^+ per litre (10 p.p.m.) can be detected thus.

Avoid an excess of HCl. $BaCl_2$ can precipitate if the solution is sufficiently strong in HCl, but it redissolves on dilution.

The presence of a coarse precipitate of Hg_2Cl_2 impedes the dissolution of small quantities of AgCl in NH_3, since the AgCl is reduced and is converted to silver amalgam.

THALLIUM

$$Tl = 204.4$$

States of oxidation.—I and III. The latter state classes the element with the ammonia group, whilst in the former it resembles the alkalis and also Ag(I). It also resembles lead: $Tl(I)/Pb(II)$, $Tl(III)/Pb(IV)$.

IIb	IIIb	IVb
	Ga(III)	
Cd(II)	In(III)	Sn(IV)
Hg(II)	Tl(III)	Pb(IV)

Tl(I)

Thallous salts.—TlOH is a strong base, white, and soluble in water. Tl_2O is brownish black. The cation is colourless.

Few complexes. None with $S_2O_3^{2-}$ (difference from Pb(II) and Ag (I)); none with NH_3 (difference from Ag^+).

The low-solubility compounds resemble those of silver and lead: the chloride more soluble in the hot, the bromide, thiocyanate, yellow iodide, yellow chromate having a low solubility in dilute acids, the black sulphide a low solubility at pH 3. The platinichloride and the cobaltinitrite resemble those of the alkali metals.

Equilibrium constants

$$
\begin{array}{llll}
TlOH \rightleftharpoons Tl^+ + OH^- & . & . & . & 0.2 \\
Tl_2CO_3 \downarrow \rightleftharpoons 2Tl^+ + CO_3^{2-} & . & . & . & 3.9 \\
TlBrO_3 \downarrow \rightleftharpoons Tl^+ + BrO_3^- & . & . & . & 3.4 \\
TlCl \downarrow \rightleftharpoons Tl^+ + Cl^- & . & . & . & 3.7 \\
TlCl \rightleftharpoons Tl^+ + Cl^- & . & . & . & 0.6 \\
TlCNS \downarrow \rightleftharpoons Tl^+ + CNS^- & . & . & . & 3.8 \\
TlIO_3 \downarrow \rightleftharpoons Tl^+ + IO_3^- & . & . & . & 5.3 \\
TlBr \downarrow \rightleftharpoons Tl^+ + Br^- & . & . & . & 5.4 \\
TlBr \rightleftharpoons Tl^+ + Br^- & . & . & . & 0.9 \\
TlI \downarrow \rightleftharpoons Tl^+ + I^- & . & . & . & 7.2 \\
Tl_2S \downarrow \rightleftharpoons 2Tl^+ + S^{2-} & . & . & . & 22.3\text{–}23.9 \\
\end{array}
$$

Tl(III)

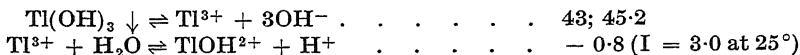**Thallic salts.** The cations are colourless: $TlOH^{2+}$ and TlO^+. Reddish-brown $Tl(OH)_3$ precipitates around pH 0.3 (0.01M). Tl_2O_3 is black.
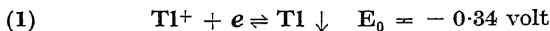
Numerous complexes, in particular chloride ones up to $TlCl_6^{3-}$, not very stable. Unstable sulphate complexes. Complexes with the anions of hydroxylated organic compounds, with F^-, $C_2O_4^{2-}$, etc.

$HTlCl_4$ is soluble in ethers.

Few of the compounds are less soluble than the hydroxide. $TlPO_4$ is one of these.

$$Tl(OH)_3 \downarrow \rightleftharpoons Tl^{3+} + 3OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 43; \ 45{\cdot}2$$

$$Tl^{3+} + H_2O \rightleftharpoons TlOH^{2+} + H^+ \quad . \quad . \quad . \quad . \quad . \quad -0{\cdot}8 \ (I = 3{\cdot}0 \ \text{at} \ 25°)$$

Redox

(1) $\qquad Tl^+ + e \rightleftharpoons Tl \downarrow \quad E_0 = -0{\cdot}34$ volt

In N-HCl, $E'_0 = -0{\cdot}55$ volt; in $N{\text{-}}H_2SO_4$, $E'_0 = -0{\cdot}33$ volt.

The metal is a fairly strong reductant, and is little attacked by conc. HCl because TlCl is not very soluble and protects the metal. It is attacked by dilute nitric and sulphuric acids.

Zinc, aluminium, and magnesium precipitate thallium from its salts.

(2) $\qquad Tl^{3+} + 2e \rightleftharpoons Tl^+ \quad E_0 = 1{\cdot}28$ volts
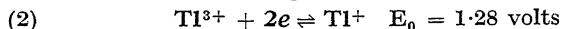
In $N{\text{-}}HNO_3 \ E'_0 = 1{\cdot}23{\text{-}}1{\cdot}26$; in $0{\cdot}1{\text{-}}1{\cdot}0N{\text{-}}H_2SO_4$, $E'_0 = 1{\cdot}21$. In $0{\cdot}6 \ N{\text{-}}HCl$, $E'_0 = 0{\cdot}78$ volt.

In acid solution, the strong oxidant Tl^{3+} easily yields Tl^+; the formation of low-solubility TlCl favours the reduction, and so Tl^{3+} partially oxidizes HCl, and completely oxidizes iodides.

$$Tl^{3+} + 3I^- \rightleftharpoons TlI \downarrow + I_2$$
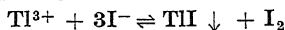
The thallous salts are only oxidized by powerful oxidants, MnO_4^-, Cl_2 in strong acid. On the other hand, Tl^+ is an energetic reductant in alkaline solution.
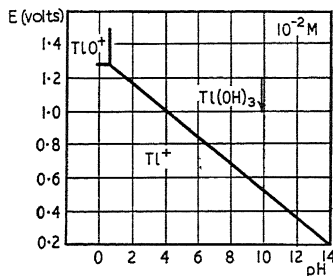
FIG. 77.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEM $Tl(III)/Tl(I)$ AS A FUNCTION OF pH

Detection of thallium.—Tl(III) and Tl(I).—Thallium can be detected in the initial solution before adding HCl. A yellow precipitate of TlI is thrown down when an iodide is added.

Solution required.—5 per cent potassium iodide.

Procedure.—Add a drop of iodide to a drop of solution in a micro-centrifuge tube.

Concentration limit.—3.10^{-4} g.-ion/litre (60 p.p.m.).

Specificity.—Ag^+, Pb^{2+}, Cu^{2+}, and Hg_2^{2+} also precipitate. The first three are complexed by the addition of a drop of tartrate (15 per cent) and a drop of 20 per cent cyanide.

Se, Te precipitate from their compounds.

Oxidants, including Tl^{3+}, precipitate iodine, which disappears in the presence of cyanide.

Note about reactions with iodides.—In dilute acid, the absence of a precipitate when iodide is added in excess indicates the absence of Tl(III) and Tl(I) 3.10^{-4}, Pb(II) 2.10^{-3}, Hg(II) 10^{-3}, Ag(I) 3.10^{-3}, Se(IV) and Te(IV), Au(III), Pd(II). Cu(II) gives a marked coloration of iodine at 5.10^{-4} and a detectable precipitate at 2.10^{-2} g.-ion/litre. Hg(II) gives a red ppt. of HgI_2 which redissolves in an excess of iodide. The iodide complexes of Bi(III) are orange (2.10^{-4} g.-ion/litre); addition of thiosulphate does not eliminate this coloration. The complexes of the metals of the platinum group are orange to brown.

Some oxidants, Fe(III), Mo(VI), etc., give iodine which disappears when a reductant is added (e.g. $S_2O_3^{2-}$, CN^-).

Note.—If the solution is a sufficiently oxidizing one, for instance if indicators, such as benzidine, are oxidized, thallium is present in the III oxidation state.

The **flame** is coloured emerald green by thallium.

The **visible spectrum** is characteristic.

THE PRECIOUS METALS

THE precious metals, gold, platinum, and the metals of the platinum group, are fairly resistant to attack, i.e. they are not at all easily oxidized.

GOLD

$$Au = 197 \cdot 2$$

States of oxidation.—I and III. The unstable AuO_2 is also known.

Au(I)

Gold is located in the periodic classification in terms of this state, in which it resembles Ag(I), Cu(I), and Hg(I). The hydroxide AuOH gives the unstable oxide Au_2O. It is a stronger base than AgOH, and is amphoteric. The ions are $Au(OH)_2^-$ or AuO^-.

The aurous salts are of low solubility like the cuprous and the mercurous. AuCl is white. The sulphide Au_2S is a black powder which decomposes into gold and sulphur.

There are numerous complexes: stable thiosulphates, extremely stable cyanides.

Equilibrium constants

$$AuOH \downarrow \rightleftharpoons Au^+ + OH^- \quad . \quad . \quad . \quad 19 \cdot 1$$
$$AuCl_2^- \rightleftharpoons Au^+ + 2Cl^- \quad . \quad . \quad . \quad 5 \cdot 5$$
$$AuBr_2^- \rightleftharpoons Au^+ + 2Br^- \quad . \quad . \quad . \quad 8$$
$$Au(CNS)_4^{3-} \rightleftharpoons Au(CNS)_2^- + 2CNS^- \quad . \quad . \quad 4 \cdot 3$$
$$Au(CNS)_2^- \rightleftharpoons Au^+ + 2CNS^- \quad . \quad . \quad . \quad 13$$
$$AuI \downarrow \rightleftharpoons Au^+ + I^- \quad . \quad . \quad . \quad . \quad 16$$
$$Au(CN)_2^- \rightleftharpoons Au^+ + 2CN^- \quad . \quad . \quad . \quad 21$$

Au(III)

The rust-coloured hydroxide $Au(OH)_3$ rapidly goes to the black Au_2O_3. Its solubility in $N-HNO_3$ is low ($10^{-5}M$), and is also low in $N-H_2SO_4$ ($10^{-4 \cdot 5}M$); in $20N-H_2SO_4$ its solubility is $0 \cdot 06M$. The cations are AuO^+. In alkalis, the anion AuO_2^- is formed.

In HCl, $Au(OH)_3$ dissolves through formation of the complexes $AuCl_4^-$, $AuCl_3OH^-$, which are yellow. Ammonia gives with the auric salts a dirty yellow precipitate of explosive gold fulminate. Hydrogen sulphide gives a precipitate of black Au_2S_3 which redissolves at pH 11 in S_2^- (brown). In the hot, Au_2S_3 disproportionates into Au and SO_4^{2-}; $HAuCl_4$ is soluble in ether.

Equilibrium constants

$$Au(OH)_3 \downarrow \rightleftharpoons Au^{3+} + 3OH^- \quad \ldots \ldots \ldots \quad 45$$
$$AuCl_4^- + H_2O \rightleftharpoons AuCl_3OH^- + Cl^- + H^+; \quad pk_4 = 6\cdot1$$
$$AuCl_3OH^- + H_2O \rightleftharpoons AuCl_2(OH)_2^- + Cl^- + H^+; \quad pk_3 = 7\cdot0;$$
$$pk_2 = 8\cdot1; \ pk_1 = 8\cdot5$$
$$AuCl_4^- \rightleftharpoons Au^{3+} + 4Cl^- \quad \ldots \ldots \quad 19; \ 21\cdot3$$
$$AuBr_4^- \rightleftharpoons Au^{3+} + 4Br^- \quad \ldots \ldots \quad 25$$
$$Au(CNS)_4^- \rightleftharpoons Au^{3+} + 4CNS^- \quad \ldots \ldots \quad 36; \ 37\cdot5$$

Redox

(1) $\qquad Au^+ + e \rightleftharpoons Au \downarrow \quad E_0 = 1\cdot46$ volts
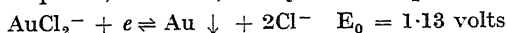
(2) $\qquad Au^{3+} + 2e \rightleftharpoons Au^+ \quad E_0 = 1\cdot39$,,
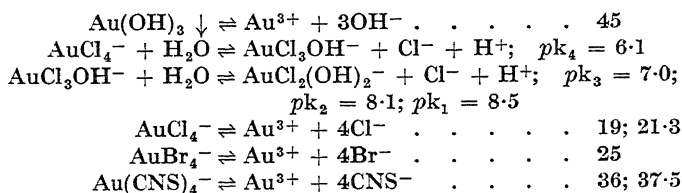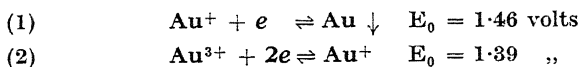
Formal potentials

In $N\text{-}H_2SO_4$ saturated with auric oxide $\quad \ldots \quad 1\cdot27$ volts

In $N\text{-}HNO_3$,, ,, ,, ,, $\quad \ldots \quad 1\cdot26$,,

In HCl: $AuCl_4^- + 2e \rightleftharpoons AuCl_2^- + 2Cl^- \quad E_0 = 0\cdot95; \ 0\cdot93$ volt

Bromide complexes, $0\cdot82$ volt, thiocyanate complexes, $0\cdot64$ volt, and

$$AuCl_2^- + e \rightleftharpoons Au \downarrow + 2Cl^- \quad E_0 = 1\cdot13 \text{ volts}$$

Thus it appears that in HCl $AuCl_2^-$ is partially disproportionated, and the system

$$AuCl_4^- + 3e \rightleftharpoons Au \downarrow + 4Cl^- \quad E_0 = 1\cdot01 \text{ volts}$$
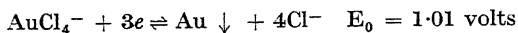
is set up. Gold is a noble metal, i.e. it is oxidizable with difficulty. It is not attacked by any systems except those whose potential is high, aqua regia for example. The salts are easy to reduce, they are oxidants like chlorine.

Ferrous and stannous ion, oxalic acid, hydrogen peroxide, all reduce the salts of gold to the metal giving a brown, red, violet or blue precipitate according to the particle size of the metal obtained. Reduction by Fe^{2+} is specific.

In alkali: $\qquad AuO_2^- + 4H^+ + 3e \rightleftharpoons Au \downarrow + 2H_2O$
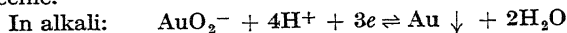
Formal potential: $0\cdot30$ volt in $7\text{--}8N\text{-}NaOH$.

(3) $\quad AuO_2 \downarrow + 4H^+ + 4e \rightleftharpoons Au \downarrow + 2H_2O \quad E_0 = 1\cdot75 \text{ volts}$

AuO_2 is not stable, because it is too oxidizing.

(4) **Aurocyanide complex**

$$Au(CN)_2^- + e \rightleftharpoons Au \downarrow + 2CN^- \quad E_0 = 0\cdot20 \text{ volt}$$
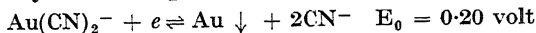
Gold dissolves in cyanide solutions in the air, and more rapidly when H_2O_2 is present.

Detection

(1) **Reduction by Fe^{2+}.**—Gold salts are reduced by ferrous ions, metallic gold being precipitated. Make the test on the water bath. The reduction can also be effected by oxalic acid and hydroquinone in the hot.

(2) **Detection of traces.**—**Purple of Cassius.**—Gold salts are reduced by stannous chloride in dilute solution to very finely divided gold. In the presence of colloidal $Sn(OH)_4$ the gold is adsorbed and a purple coloration is obtained. The same results are obtained with Ti(III).

Procedure.—To some drops of water, add a drop of stannous chloride, and then a drop of the test solution.

Concentration limit.—10^{-5} g.-ion/litre of Au(III) (2 p.p.m.).

*Interfering substances.*—These are very numerous (see p. 220). The metals of the platinum group in particular are precipitated.

PLATINUM AND METALS OF THE PLATINUM GROUP

Ru $=101\cdot7$; Rh $=102\cdot9$; Pd $=106\cdot7$; Os $=191\cdot5$; Ir $=193\cdot1$; Pt $=195\cdot2$

General properties.—The metals are not easily oxidizable. They give alloys which are more or less easily attacked. Aqua regia attacks them because of complex formation, and molten caustic potash also attacks all of them.

The finely divided metals catalyse the majority of the reactions of the redox systems of water and principally:

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow$$
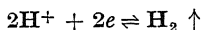
Reductants like hypophosphorous acid, chromous salts, can then react at a considerable rate on H ions giving $H_2 \uparrow$. In their presence O_2 oxidizes more rapidly. They also catalyse numerous other redox reactions: oxidation of CO, of oxalates, formates, etc.

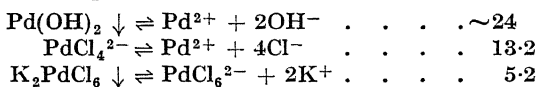There are numerous cyanide, ammine, oxalate, thiocyanate, thiosulphate, chloride and sulphate complexes.

The metals can exist in several states of oxidation.
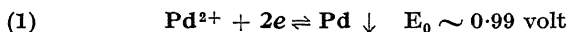
PALLADIUM

States of oxidation.—IV and II. II is the more important.

Palladous salts.—The solutions are brown or red; reddish-brown $Pd(OH)_2$ precipitates around pH $3\cdot3$ and develops rapidly; it dissolves in very alkaline solution. The solubility of black PdI_2 is very low, but it dissolves in an excess of iodide to give a deep brown solution. PdS is black. Palladium cyanide $Pd(CN)_2$ is yellow; its solubility is low. Palladium acetylide PdC_2, obtained by the action of acetylene on the palladous salts, is pale yellow and of low solubility. Palladium dimethylglyoxime is yellow, of low solubility in neutral or fairly weak acid solution. $(NH_4)_2PdCl_4$ is soluble. $(NH_4)_2PdCl_6$ is of low solubility.

Very stable complexes are formed with NH_3, CN^-, NO_2^-, etc.

$$Pd(OH)_2 \downarrow \rightleftharpoons Pd^{2+} + 2OH^- \quad . \quad . \quad . \quad . \sim 24$$
$$PdCl_4{}^{2-} \rightleftharpoons Pd^{2+} + 4Cl^- \quad . \quad . \quad . \quad . \quad 13\cdot2$$
$$K_2PdCl_6 \downarrow \rightleftharpoons PdCl_6{}^{2-} + 2K^+ . \quad . \quad . \quad . \quad 5\cdot2$$

Redox

(1) $\qquad Pd^{2+} + 2e \rightleftharpoons Pd \downarrow \quad E_0 \sim 0\cdot99$ volt

In HCl:

$$PdCl_4{}^{2-} + 2e \rightleftharpoons Pd \downarrow + 4Cl^- \quad E_0 = 0\cdot62 \text{ volt}$$
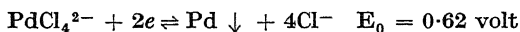
The formal potential is $- 0\cdot1$ volt, in $0\cdot1$M-CN^-.

Conc. HNO_3 attacks palladium, giving a deep red solution. Hot conc. H_2SO_4 also attacks the metal. The finely divided metal is oxidized in the air in conc. HCl. Aqua regia attacks it, yielding Pd(II).

The finely divided metal has the property of adsorbing large quantities of hydrogen; it then catalyses the reaction:

$$H_2 - 2e \rightleftharpoons 2H^+$$
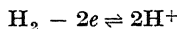
Pd(II) is reduced to the metal by SO_2, Fe^{2+}, alcohol, etc.

(2) $\qquad Pd^{4+} + 2e \rightleftharpoons Pd^{2+} \qquad\qquad E_0 \sim 1\cdot 6$ volts
$\qquad\qquad PdCl_6{}^{2-} + 2e \rightleftharpoons PdCl_4{}^{2-} + 2Cl^- \qquad E_0 = 1\cdot 30$,,
$Pd(OH)_4 \downarrow + 2H^+ + 2e \rightleftharpoons Pd(OH)_2 \downarrow + 2H_2O \quad E_0 \sim 0\cdot 8$ volt

Palladous salts are more stable than the palladic ones.

Detection

Iodide ions give black PdI_2, soluble in excess to give a deep red solution. Numerous ions interfere.

Concentration limit.—5.10^{-5} g.-ion of Pd(II) per litre (5 p.p.m.).
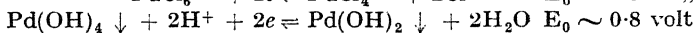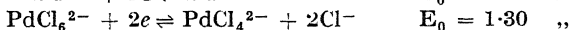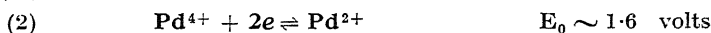
Stannous ions give a violet-black coloration (see platinum). Numerous ions interfere (see p. 220).

Concentration limit.—5.10^{-4} (50 p.p.m.).

Dimethylglyoxime.—In acid solution, DMG gives a yellow precipitate of palladium-DMG (see nickel, p. 196).

Concentration limit.—10^{-3} g.-ion/litre, or 100 p.p.m.
Interfering substances.—The other congeners of platinum do not interfere. Gold precipitates by reduction of the reagent.

In the presence of nickel carry out the test in $0\cdot2$–$1\cdot5$N-HCl at the boil. Ni(II) does not precipitate.

PLATINUM

States of oxidation.—II and IV, the latter is the more stable. VI is represented by the unstable PtO_3.

Pt(II)

The freshly precipitated hydroxide $Pt(OH)_2$ is soluble in HNO_3 and conc. H_2SO_4. It develops rapidly and then its solubility in these acids becomes low; it is scarcely soluble in NaOH.

Black PtS is soluble in sulphides and gives reddish-brown anions. PtI_2, brownish black, has a low solubility.

Numerous complexes: $PtCl_4{}^{2-}$ red, $Pt(NO_2)_4{}^{2-}$, $Pt(CN)_4{}^{2-}$, $Pt(C_2O_4)_2{}^{2-}$, $Pt(CNS)_4{}^{2-}$ red, etc.

$$Pt(OH)_2 \downarrow \rightleftharpoons Pt^{2+} + 2OH^- \quad . \quad . \quad . \quad . \quad \sim 35$$
$$PtCl_4{}^{2-} \rightleftharpoons Pt^{2+} + 4Cl^- \quad . \quad . \quad . \quad . \quad \sim 16$$
$$PtBr_4{}^{2-} \rightleftharpoons Pt^{2+} + 4Br^- \quad . \quad . \quad . \quad . \quad \sim 18$$
$$PtS \downarrow \rightleftharpoons Pt^{2+} + S^{2-} \quad . \quad . \quad . \quad . \quad . \quad \sim 70$$
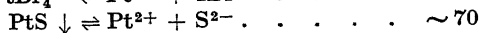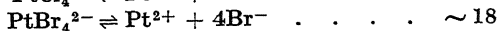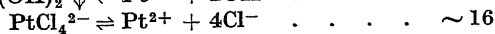
Pt(IV)

The freshly formed hydroxide $H_2Pt(OH)_6$ is white (it may also be represented as $Pt(OH)_4$). Only slightly soluble in 2N-HNO_3 and H_2SO_4, soluble in alkalis giving the anion $Pt(OH)_6{}^{2-}$, and in NH_3 giving ammines. In HCl, orange $PtCl_6{}^{2-}$ is formed. The sulphide PtS_2, brownish black, is

of low solubility in acids, and difficultly soluble in alkalis. Pt(IV) is met with almost entirely as complexes such as the platinichloride ion $PtCl_6^{2-}$. Ammonium and potassium platinichlorides are of low solubility; when ignited, they yield platinum.

The complexes are very numerous. The cyanide complexes are very stable and are colourless. PtI_6^{2-} reddish brown, $Pt(CN)_6^{2-}$, $Pt(N_3)_2^{2-}$, $Pt(NO_2)_6^{2-}$, etc.

$$K_2PtCl_6 \downarrow \rightleftharpoons PtCl_6^{2-} + 2K^+ \quad . \quad . \quad . \quad . \quad . \quad 5$$
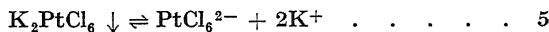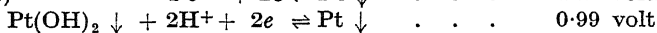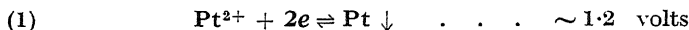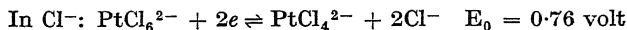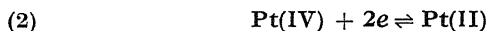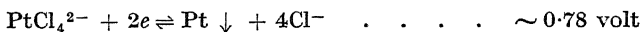
Redox

(1) $\qquad\qquad Pt^{2+} + 2e \rightleftharpoons Pt \downarrow \quad . \quad . \quad . \quad \sim 1\cdot 2$ volts

$\quad Pt(OH)_2 \downarrow + 2H^+ + 2e \rightleftharpoons Pt \downarrow \quad . \quad . \quad . \quad 0\cdot 99$ volt

In Cl^- solution:

$\quad PtCl_4^{2-} + 2e \rightleftharpoons Pt \downarrow + 4Cl^- \quad . \quad . \quad . \quad . \quad \sim 0\cdot 78$ volt

(2) $\qquad\qquad Pt(IV) + 2e \rightleftharpoons Pt(II)$

In Cl^-: $PtCl_6^{2-} + 2e \rightleftharpoons PtCl_4^{2-} + 2Cl^- \quad E_0 = 0\cdot 76$ volt

(Bromide complexes, $E_0 = 0\cdot 65$ volt.)

Thus, in Cl^- the oxidation state II is disproportionated, at any rate partially.

Platinum, as well as other metals of the platinum group, is a 'noble' metal attacked with difficulty by oxidants, unless complexes (e.g. with Cl^-) are formed (aqua regia). Finely divided, e.g. when alloyed with a relatively small proportion of silver, it is attacked by HNO_3.

The salts are easily reduced, but less easily than gold salts. Thus, oxalic acid, ferrous salts, and SO_2 do not reduce them in HCl (difference from gold). Fe, Zn, Al, HCHO, in alkaline solution, precipitate platinum as a black powder.

Detection.—(1) **Stannous chloride** gives a reddish-orange coloration. Numerous ions interfere. Concentration limit 2.10^{-5} g.-ion/litre.

(2) **Iodides** give a brownish-pink coloration of PtI_6^{2-}, 10^{-4}. Numerous ions interfere (see p. 247).

RUTHENIUM

States of oxidation.—All from I–IV, VI, and VIII.

Ru(VIII).—The oxide is RuO_4, volatile and toxic; gives a yellow solution in water. The dissolved oxide gradually decomposes to RuO_2. Chloride complexes are known.

Ru(VI).—In acids, chloride complexes such as $RuO_2Cl_4^{2-}$. In alkaline solution, orange ruthenates, RuO_4^{2-}, are formed; they are unstable and slowly disproportionate, forming RuO_2.

Ru(IV).—Deep reddish-orange chloride complexes. They are reduced to Ru(III) by numerous reductants (I^-, Fe^{2+}), etc.

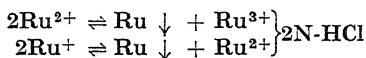**Ru(III).**—Numerous complexes, chloride, ammine, oxalate, etc. $Ru(OH)_3$, which is brownish black, is of low solubility in alkaline solution. It precipitates from $RuCl_5^{2-}$ at pH 3·2–3·5.

Ru(II).—Deep blue.

Redox

$$Ru \downarrow - 3e \rightleftharpoons Ru^{3+} \quad . \quad . \quad . \quad . \quad 0.9 \text{ volt}$$
$$Ru(V) + e \rightleftharpoons Ru(IV) \quad . \quad . \quad . \quad . \quad 1.40 \text{ volts in N-HClO}_4$$
$$Ru(IV) + e \rightleftharpoons Ru(III) \quad . \quad . \quad . \quad . \quad 0.87 \text{ volt in N-HCl}$$
$$Ru(III) + e \rightleftharpoons Ru(II) \quad . \quad . \quad . \quad . \quad 0.7 \quad ,, \quad ,, \quad ,,$$
$$Ru(II) + e \rightleftharpoons Ru(I) \quad . \quad . \quad . \quad . \quad 0.04 \quad ,, \quad ,, \quad N/10\text{-HCl}$$

Reduction by titanous sulphate yields Ru(II). It oxidizes slowly in the air. The following disproportionation reactions occur:

$$\left.\begin{array}{l} 2Ru^{2+} \rightleftharpoons Ru \downarrow + Ru^{3+} \\ 2Ru^+ \rightleftharpoons Ru \downarrow + Ru^{2+} \end{array}\right\} 2N\text{-HCl}$$

Zinc in hot acetic acid gives Ru.

Powerful oxidants like MnO_4^- give the volatile RuO_4, which is reduced by conc. HCl, giving Ru(IV) and, slowly, Ru(III).

The metal is attacked with difficulty by strong acids in the presence of ClO_3^- giving RuO_4^-; it is generally brought into solution by oxidizing alkaline fusion.

OSMIUM

States of oxidation.—III, IV, VI, VIII.

Os(VIII).—OsO_4 is volatile, toxic, soluble in the cold; H_2OsO_5, bright yellow, is known, $pk = 12.1$.

Attacking the metal with molten KOH gives the osmate ion OsO_4^{2-} which in acids disproportionates into OsO_4 and $Os(OH)_4$. Powerful oxidants end up by producing OsO_4. Os(VIII) can be reduced by iodides to $Os(OH)_4$; HCl yields $OsCl_6^{2-}$. Sn(II) reduces it to the metal.

Os(IV).—$Os(OH)_4$ brown, $OsCl_6^{2-}$.

$Os/OsCl_6^{2-}$, E $= 0.44$ volt in dilute acid.

RHODIUM

States of oxidation.—III, IV, VI.

Rh(VI).—The rhodates, RhO_4^{2-}, deep violet.

Rh(IV).—The hydroxide $Rh(OH)_4$ is soluble in acetic acid to give a blue solution and in potash to give a deep green one.

Rh(III).—This is the most important state of oxidation. Hydrated Rh_2O_3 is yellow, brownish black in the hot, and soluble in acids; freshly precipitated, it dissolves in conc. KOH but is precipitated on dilution.

$RhCl_6^{3-}$ precipitates at pH 6.6.

There are numerous complexes: $Rh(OH)_3Cl_3^{3-}$ reddish brown, $RhCl_6^{3-}$ yellow.

$$RhCl_6^{3-} \rightleftharpoons Rh^{3+} + 6Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 12$$

$Rh(C_2O_4)_3^{3-}$, $Rh(CNS)_3$ orange, $Rh(CNS)_6^{3-}$ garnet, $Rh(CN)_6^{3-}$.

Numerous ammines.

Redox.—Rh(IV)/Rh(III), E $= 1.42$ volts in $N\text{-}H_2SO_4$ (sulphate complexes). Rh(VI)/Rh(IV), E $= 1.44$ volts in $0.2N\text{-}H_2SO_4$. Rh(IV) thus disproportionates easily:

$$3Rh(IV) \rightarrow Rh(VI) + 2Rh(III)$$
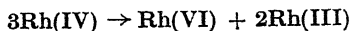
Reduction of Rh(VI) nearly always yields Rh(III). However, if HF is used, a halt can be called at the state IV as a result of complex formation.

$$RhCl_6^{3-} + 3e \rightleftharpoons Rh \downarrow + 6Cl^- \quad . \quad . \quad . \quad 0.64 \text{ volt}$$
$$Rh(VI) + 3e \rightleftharpoons Rh(III) \quad . \quad . \quad . \quad . \quad 1.46 \text{ volts}$$

$Rh(CN)_6^{3-}$ and $Rh(NH_3)_5Cl^{2+}$, very stable, are not oxidizable, even electrolytically.

$Rh/Rh(III)$, $E = 0.7$ volt in N-HCl, and 0.80 volt in N-HClO, 0.7 volt in H_2SO_4. The massive metal is not attacked by aqua regia, but is so when divided. Molten KOH gives Rh_2O_3.

IRIDIUM

States of oxidation.—III, IV, VI.

Ir(III).—$IrCl_6^{3-}$ is brown to green; NaOH precipitates $Ir(OH)_3$, black, at pH 7·5, which oxidizes slowly in the air.

Numerous complexes. $Ir(CN)_6^{3-}$, $Ir(CNS)_3$, $Ir(C_2O_4)_3^{3-}$, ammines.

$$\tfrac{1}{2}Ir_2O_3 \downarrow + \tfrac{3}{2}H_2O \rightleftharpoons Ir^{3+} + 3OH^- \quad . \quad . \quad . \quad \sim 45$$
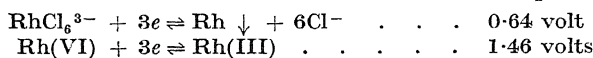$$IrCl_6^{3-} \rightleftharpoons Ir^{3+} + 6Cl^- \quad . \quad . \quad . \quad . \quad \sim 14$$
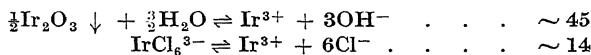
Ir(IV).—IrO_2 dissolves slightly in conc. HNO_3 to give a blue solution, and dissolves very slightly in alkalis. $IrCl_6^{3-}$, reddish brown, precipitates at pH 7.

Redox.—The metal is not attacked by aqua regia; when alloyed with platinum, the attack is slow. Molten KOH forms the iridate anion IrO_4^{2-}.

$$IrCl_6^{3-} - e \rightleftharpoons IrCl_6^{2-} \quad E_0 = 1.02 \text{ volts}$$
$$Ir \downarrow + 6Cl^- - 3e \rightleftharpoons IrCl_6^{3-} \quad E_0 = 0.72 \text{ volt}$$

IONS DERIVED FROM THE HALOGENS.
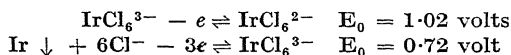
FLUORINE. CHLORINE. BROMINE. IODINE

	VII

O^{2-}	F^-
S^{2-}	Cl^-
	Br^-
	I^-

THE halogens are to be found in the seventh group of the periodic table.

States of oxidation.—Almost all from I^- to VII^+ are represented. The anions I^- are more and more basic in the direction of the arrows in the table alongside. Among the halogens, only F^- is basic, $pk = 3.2$. HCl, HBr, HI are strong acids completely ionized. F^- differs from the three others in particular in its poorly ionized compounds.

Redox

$$O_2 + 4e \rightleftharpoons 2O^{2-} \quad . \quad . \quad . \quad . \quad . \quad 0.26 \text{ volt}$$
$$F_2 + 2e \rightleftharpoons 2F^- \quad . \quad . \quad . \quad . \quad . \quad 2.85 \text{ volts}$$
$$Cl_2 + 2e \rightleftharpoons 2Cl^- \quad . \quad . \quad . \quad . \quad . \quad 1.41 \quad ,,$$
$$Br_2 + 2e \rightleftharpoons 2Br^- \quad . \quad . \quad . \quad . \quad . \quad 1.09 \quad ,,$$
$$I_2 + 2e \rightleftharpoons 2I^- \quad . \quad . \quad . \quad . \quad . \quad 0.62 \text{ volt}$$

For the fictitious concentrations $|\,O_2\,|$, $|\,F_2\,|$, etc. $= 1$.

FLUORINE

$$F = 19.00$$

Only one state of oxidation—I^-.

Influence of pH.—In concentrated solution, H_2F_2 is present; the first acidity is strong: $H_2F_2 \rightarrow HF_2^- + H^+$.

HF_2^- is a complex of low stability:

$$\frac{|\,HF\,|.|\,F^-\,|}{|\,HF_2^-\,|} = 0.19; \quad pk = -0.7$$

In dilute solution, we thus have

$$HF \rightleftharpoons H^+ + F^-; \quad pk = 3.2$$

Properties of HF.—It boils at 19°. It is miscible with water, toxic, and corrosive. With water it gives an azeotrope which boils at 120°, and whose strength is approximately 12N.

It attacks SiO_2, giving, in the absence of water, gaseous SiF_4.

$$SiO_2 \downarrow + 4HF \rightarrow SiF_4 \uparrow + 2H_2O$$

$SiOF_2$, a solid, can also be produced.

Silicon fluoride reacts with water to give hydrofluosilicic acid, and gelatinous silica.

$$3SiF_4 \uparrow + 4H_2O \rightarrow 2SiF_6^{2-} + 4H^+ + Si(OH)_4 \downarrow$$

From aqueous solution, H_2SiF_6 distils with water.

HF can only be handled in vessels of platinum, silver, or of some

plastics. When converted to the form of fairly stable complexes, such as borate ones or those with Al(III), the attack on glass ceases.

Low-solubility compounds.—A certain number of fluorides are soluble, among which are those of the alkali metals and silver. The solubility of the majority is low, but they dissolve in strong acids. The fluorides of ions of elements in the IV oxidation state, and those of the rare earths, have a low solubility in strong acids; some of them can be considered as salts of strong acids: $Ce[CeF_6]$; or of fairly strong acids: $Al[AlF_6]$.

Complexes.—Complexes are extremely numerous with ions whose oxidation numbers are III, IV, VI. The most stable are those with Al(III), Be(II), Sn(IV), Zr(IV). Fairly stable ones are formed with B(III): BF_4^-, BF_3OH^-. Relatively unstable complexes with Si(IV), e.g. $(SiF_6)^{2-}$. A certain number of complexes give low-solubility salts:

$$Na_3AlF_6, \quad Na_3FeF_6, \quad Na_2ThF_6$$
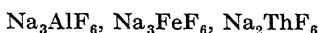
Equilibrium constants

$$HF_2^- \rightleftharpoons HF + F^- \quad \ldots \ldots \ldots \quad -0.7$$
$$HF \rightleftharpoons H^+ + F^- \quad \ldots \ldots \ldots \quad 3.2$$
$$LiF \downarrow \rightleftharpoons Li^+ + F^- \quad \ldots \ldots \ldots \quad 2.3$$
$$BaF_2 \downarrow \rightleftharpoons Ba^{2+} + 2F^- \quad \ldots \ldots \ldots \quad 5.8$$
$$PbF_2 \downarrow \rightleftharpoons Pb^{2+} + 2F^- \quad \ldots \ldots \ldots \quad 7.4$$
$$MgF_2 \downarrow \rightleftharpoons Mg^{2+} + 2F^- \quad \ldots \ldots \ldots \quad 8.2$$
$$SrF_2 \downarrow \rightleftharpoons Sr^{2+} + 2F^- \quad \ldots \ldots \ldots \quad 8.5$$
$$CaF_2 \downarrow \rightleftharpoons Ca^{2+} + 2F^- \quad \ldots \ldots \ldots \quad 10.4$$
$$AlF_6^{3-} \rightleftharpoons AlF_5^{2-} + F^-; \quad pk_6 = 0.5; \ pk_5 = 1.6; \ pk_4 = 2.7;$$
$$AlF_3 \downarrow; \ pk_3 = 3.85; \ pk_2 = 5.0; \ pk_1 = 6.1$$
$$Al[AlF_6] \downarrow \rightleftharpoons Al^{3+} + AlF_6^{3-} \ . \ \ldots \ldots \ldots \quad 9.4$$
$$Na_3[AlF_6] \downarrow \rightleftharpoons 3Na^+ + AlF_6^{3-} \quad \ldots \ldots \ldots \quad \sim 27$$
$$FeF_5^{2-} \rightleftharpoons FeF_4^- + F^-; \quad pk_5 = 0.5; \ pk_4 = 2.2; \ pk_3 = 3.0;$$
$$pk_2 = 4.2; \ pk_1 = 5.5 \ (I = 0.5)$$
$$BeF^+ \rightleftharpoons Be^{2+} + F^- \ . \ \ldots \ldots \ldots \quad 4.3; \ 5.2$$
$$SiF_6^{2-} \rightleftharpoons SiF_4 + 2F^- \quad \ldots \ldots \ldots \quad 7.2$$
$$SiF_4 + 2H_2O \rightleftharpoons SiO_2 \downarrow + 4HF \quad \ldots \ldots \ldots \quad 8$$
$$HBF_4 + H_2O \rightleftharpoons HBF_3OH + HF \quad \ldots \ldots \ldots \quad 2.6$$
$$HBF_3OH + H_2O \rightleftharpoons HBF_2(OH)_2 + HF \quad \ldots \ldots \ldots \quad 2.0$$
$$ThF_4 \downarrow \rightleftharpoons ThF_3^+ + F^-; \quad pk_4 = 8.8; \ pk_3 = 4.7; \ pk_2 = 6.1;$$
$$pk_1 = 7.8; \ pk_4 + pk_3 + pk_2 + pk_1 = 27.4$$
$$(I = 0.5); \ 28.1$$
$$ZrF_3^+ + H^+ \rightleftharpoons ZrF_2^{2+} + HF; \quad pk_3 = 2.8; \ pk_2 = 4.3; \ pk_1 = 5.8$$

Redox

$$F_2 + 2e \rightleftharpoons 2F^- \ . \ \ldots \ . \quad +2.85 \text{ volts (calculated)}$$

Fluorine is the strongest oxidant known. It can only be prepared by dry electrolysis. It reacts with all systems, in particular with water giving oxygen and ozone:

$$F_2 \uparrow + H_2O \rightleftharpoons 2HF + \tfrac{1}{2}O_2 \uparrow$$
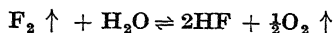
on SO_4^{2-} to give $S_2O_8^{2-}$, on Co^{2+}, Ag^+, etc.

Detection

(1) **Attack on glass.**—(*a*) Place the substance to be examined in a platinum or lead vessel and mix with conc. H_2SO_4. Cover the vessel with a watch glass, a part of which has been waxed. The unprotected parts are etched by the HF. Leave for several hours in the cold or $\frac{1}{2}$-hour in the hot.

Substances which complex F^- strongly, such as Al^{3+}, hold up small quantities of F^-. Silicon and boron interfere giving H_2SiF_6 and HBF_4.

(*b*) Clean a small test-tube with a chromic-sulphuric acid mixture in the hot. Rinse. Introduce $\frac{1}{2}$ ml of conc. H_2SO_4. Make sure that the acid wets the glass uniformly. Add several drops of the solution being examined or a particle of the solid. If fluoride is present, the walls of the tube will not be wetted. The reaction is specific, but substances which complex F^- interfere, at any rate when the F^- is present in small concentration.

Hot conc. H_3PO_4 also attacks glass.

(2) **Silicon fluoride.**—The apparatus shown in fig. 92*a*, page 326, can be used. Mix 0·2 g of silica with 0·1 g of the substance to be examined, followed by $\frac{1}{2}$ ml of conc. H_2SO_4. Heat for 30 minutes on the water bath. SiF_4 and H_2SiF_6, if formed, react on a drop of water at the end of the interior tube, and a deposit of silica is formed.

Compounds which hold up F^-: B(III), Al(III), etc., reduce the sensitivity.

(3) **Complex with zirconium.**—Salts of zirconium give with alizarin S (and also with alizarin) a red coloration (see p. 79). F^- ions cause this coloration to disappear as a result of the formation of stable complexes with Zr(IV).

Materials required.—0·05 g of zirconium nitrate and 50 ml. of 12N-HCl.
    0·05 g alizarin S in 50 ml of water.
    Mix equal quantities of the two solutions just before use.

Procedure.—Add a drop of the solution being examined to a drop of the reagent. The latter is decolorized. The final colour is yellow (of alizarin S in acid solution).

Concentration limit.—10^{-4} g.-ion of F^- per litre (2 p.p.m.).

Interfering substances.—(1) The solution should be sufficiently acid to avoid complete precipitation of $Zr(OH)_4$. Also the addition of basic anions, CO_3^{2-}, etc., should be counteracted by the addition of acid.

(2) Oxidants: ClO_3^-, BrO_3^-, IO_3^-, $Cr_2O_7^{2-}$, H_3AsO_4, HClO, can destroy the dye. These can be reduced beforehand by addition of an equal volume of 10 per cent KNO_2. Conc. HNO_3 must be avoided. Sulphites decolorize the solution slowly. They are oxidized by nitrites.

(3) Anions which complex Zr(IV), in particular $C_2O_4^{2-}$, give the same reaction. They can be got rid of by prior ignition of the solid. Large quantities of SO_4^{2-} diminish the sensitivity. They can be eliminated with Ba^{2+}.

Cations which complex F^- diminish the sensitivity or inhibit the reaction according to their concentration and the stability of the corresponding complex. This is the case with Al(III), Be(II), Sn(IV). Si(IV) and B(III) do not interfere.

Compounds which precipitate Zr(IV) in acid solution can interfere and decolorize the solution: H_3PO_4, H_3AsO_4 in excess.

General note.—The reactions can be carried out to detect certain solid fluorides; phosphates then interfere little. Heat. But natural fluorides are particularly difficult to attack. It is then necessary to break down the mineral in the dry way before making the test. However, in numerous cases, it is sufficient to attack it with hot HCl in the presence of boric acid which takes F^- into solution as a complex. The reaction can then be carried out.

Analogous reactions can be utilized for the detection of F^-. For example morin, which gives a fluorescence with zirconium (p. 179), $Fe(CNS)^{2+}$, TiO^{2+}, etc.

CHLORINE—BROMINE—IODINE

$$Cl = 35.46; \; Br = 79.9; \; I = 126.9$$

States of oxidation.—In principle, all from I^- to VII^+.

Below are given the values of the potentials calculated for the different systems:

		volts		volts		volts
I^-/O	$Cl^-/Cl_2 \uparrow$	1·36	$Br^-/Br_2 \uparrow$	1·07	$I^-/I_2 \downarrow$	0·53
O/I	$Cl_2 \uparrow /HClO$	1·63	$Br_2 \uparrow /HBrO$	1·59	$I_2/HIO \downarrow$	1·45
I/II	$HClO/HClO_2$	1·63			$I_2/H_2I_2O_3$	—
II/III					$I_2/HIO_2 \downarrow$	—
III/IV	$HClO_2/ClO_2$	1·26	$HBrO/BrO_3^-$	1·49	$I_2/IO_2 \downarrow$	—
IV/V	ClO_2/ClO_3^-	1·15			IO_3^-/HIO	1·13
V/VI	ClO_3^-/ClO_4^-	1·19			H_5IO_6/IO_3^-	1·7
VI/VII						

It can easily be seen that the majority of these compounds are not in stable equilibrium. They should disproportionate. Some should only exist in aqueous solutions, ClO_4^- and Cl^-; Br^-, Br_2, and BrO_3^-; I^-, I_2, IO_3^-, H_5IO_6 all at pH 0. However, many compounds are stable for extremely long periods of time.

ELEMENTS

Chlorine is a yellowish-green gas. Its solubility in N-HCl is 0·1M.

Bromine is a deep red liquid which gives off reddish-brown vapours. Its solubility is 0·1M. More soluble in the presence of Cl^- as a result of the formation of Br_2Cl^-, and in that of Br^- due to the formation of Br_3^- and Br_5^-. Its solubility is 0·4M in 0·4M-NaCl and 1·4M in M-KBr.

Iodine is a greyish-black solid. Its vapour is violet. Solubility 2.10^{-3}M. In the presence of I^-, the solubility increases as a result of the formation of complexes, principally I_3^-, I_2Cl^-, I_2Br^-, etc. HI_3 is a stronger acid than HI. Solubility of iodine in 6N-HCl is 0·03M.

Bromine is soluble in CCl_4, giving a brown, iodine giving a violet and chlorine a colourless solution.

When the pH increases, halogens disappear by disproportionation. This occurs between pH 3–6 for Cl_2, 6·5–9 for Br_2, and 9·5–11 for I_2.

$$Cl_2 + H_2O \rightleftharpoons HClO + Cl^- + H^+$$
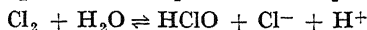
Oxidation State I⁻

Chlorides, Bromides, and Iodides

Hydracids.—Gases which fume in air, colourless, very soluble in water up to about 20M. The solutions yield constant-boiling mixtures on distillation. Strong acids. HI is stronger than HBr, and the latter stronger than HCl. The anions are colourless.
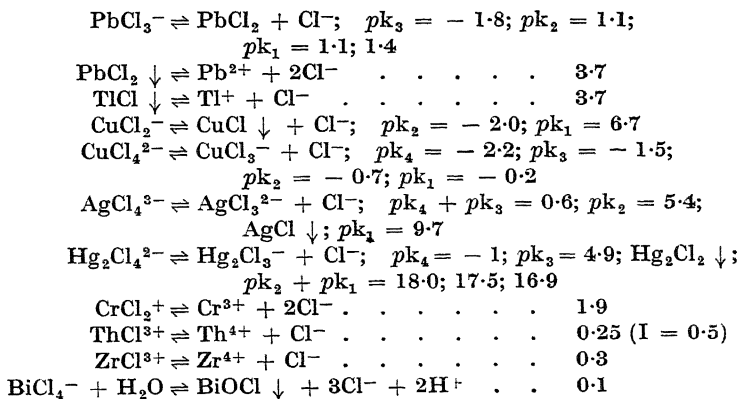
Low-solubility compounds.—The majority of the halides are soluble. Among the low-solubility compounds are the halides of Pb(II), Tl(I), Cu(I), Ag(I), Hg(I). The iodides are less soluble than the bromides, and the latter are less soluble than the chlorides. White $PbCl_2$, $PbBr_2$ and yellow PbI_2 are more soluble in the hot: they crystallize in shining leaflets on cooling. The solubility of vermilion HgI_2 and black PdI_2 is low. A certain number of basic chlorides, bromides, and iodides are also of low solubility: HgO, $HgCl_2$, SbOCl, BiOCl, $MgOCl_2$, but the majority of them redissolve in strong acid whereas the solubility of the normal halides is independent of pH except in the presence of HCl, when complexes are formed. Only AgCl is insoluble in aqua regia.

Complexes.—They are very numerous and, in general, those with Cl^- are not stable, whilst those with I^- are much more stable. The ions whose oxidation number is III, IV, and VI in general give complexes. Their stability is the same in very acid solution. Orange $PtCl_6{}^{2-}$, orange-brown $I_3{}^-$, colourless $HgI_4{}^{2-}$, yellow $ICl_2{}^-$, yellow ferric and cupric, blue cobaltous, orange Bi(III) iodides, etc.

A certain number of the soluble halides are not much ionized: for example the chlorides of cadmium (II), mercury (II), lead (II) and thallium (III).

Organic solvents.—Numerous chlorides are soluble in fairly concentrated ethereal HCl: Fe(III), Ga(III), Au(III), Tl(III), As(III), Sn(IV), etc.

Equilibrium constants

$$PbCl_3{}^- \rightleftharpoons PbCl_2 + Cl^-; \quad pk_3 = -1·8; \ pk_2 = 1·1;$$
$$pk_1 = 1·1; \ 1·4$$
$$PbCl_2 \downarrow \rightleftharpoons Pb^{2+} + 2Cl^- \quad . \quad . \quad . \quad . \quad 3·7$$
$$TlCl \downarrow \rightleftharpoons Tl^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 3·7$$
$$CuCl_2{}^- \rightleftharpoons CuCl \downarrow + Cl^-; \quad pk_2 = -2·0; \ pk_1 = 6·7$$
$$CuCl_4{}^{2-} \rightleftharpoons CuCl_3{}^- + Cl^-; \quad pk_4 = -2·2; \ pk_3 = -1·5;$$
$$pk_2 = -0·7; \ pk_1 = -0·2$$
$$AgCl_4{}^{3-} \rightleftharpoons AgCl_3{}^{2-} + Cl^-; \quad pk_4 + pk_3 = 0·6; \ pk_2 = 5·4;$$
$$AgCl \downarrow; \ pk_1 = 9·7$$
$$Hg_2Cl_4{}^{2-} \rightleftharpoons Hg_2Cl_3{}^- + Cl^-; \quad pk_4 = -1; \ pk_3 = 4·9; \ Hg_2Cl_2 \downarrow;$$
$$pk_2 + pk_1 = 18·0; \ 17·5; \ 16·9$$
$$CrCl_2{}^+ \rightleftharpoons Cr^{3+} + 2Cl^- \quad . \quad . \quad . \quad . \quad . \quad 1·9$$
$$ThCl^{3+} \rightleftharpoons Th^{4+} + Cl^- \quad . \quad . \quad . \quad . \quad 0·25 \ (I = 0·5)$$
$$ZrCl^{3+} \rightleftharpoons Zr^{4+} + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 0·3$$
$$BiCl_4{}^- + H_2O \rightleftharpoons BiOCl \downarrow + 3Cl^- + 2H^+ \quad . \quad . \quad 0·1$$

18

$$BiOCl \downarrow \rightleftharpoons BiO^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 8 \cdot 2; \ 9 \cdot 2$$

$$AuCl_4^- + H_2O \rightleftharpoons AuCl_3OH^- + Cl^- + H^+; \quad pk_4 = 6 \cdot 1$$

$$AuCl_3OH^- + H_2O \rightleftharpoons AuCl_3(OH)_2^- + Cl^- + H^+; \quad pk_3 = 7 \cdot 0;$$
$$pk_2 = 8 \cdot 1; \ pk_1 = 8 \cdot 5$$

$$AuCl_4^- \rightleftharpoons Au^{3+} + 4Cl^- \quad . \quad . \quad . \quad . \quad 19; \ 21 \cdot 3$$

$$SnCl_4^{2-} \rightleftharpoons SnCl_3^- + Cl^-; \quad pk_4 = -0 \cdot 5; \ pk_3 = -0 \cdot 2;$$
$$pk_2 = 0 \cdot 7; \ pk_1 = 1 \cdot 5$$

$$FeCl^{2+} \rightleftharpoons Fe^{3+} + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 1 \cdot 4$$

$$FeCl^+ \rightleftharpoons Fe^{2+} + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 0 \cdot 3$$

$$HgCl_4^{2-} \rightleftharpoons HgCl_3^- + Cl^-; \quad pk_4 = 0 \cdot 7; \ pk_3 = 1 \cdot 0;$$
$$pk_2 = 6 \cdot 9; \ pk_1 = 7 \cdot 15$$

$$I_2Cl^- \rightleftharpoons I_2 + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 0 \cdot 3; \ 0 \cdot 5$$

$$ICl_2^- \rightleftharpoons ICl + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 2 \cdot 2$$

$$Br_2Cl^- \rightleftharpoons Br_2 + Cl^- \quad . \quad . \quad . \quad . \quad . \quad 0 \cdot 1$$

$$IrCl_6^{3-} \rightleftharpoons Ir^{3+} + 6Cl^- \quad . \quad . \quad . \quad . \quad \sim 14$$

$$PdCl_4^{2-} \rightleftharpoons Pd^{2+} + 4Cl^- \quad . \quad . \quad . \quad . \quad 13 \cdot 2$$

$$PtCl_4^{2-} \rightleftharpoons Pt^{2+} + 4Cl^- \quad . \quad . \quad . \quad . \quad \sim 16$$

$$RhCl_6^{3-} \rightleftharpoons Rh^{3+} + 6Cl^- \quad . \quad . \quad . \quad . \quad \sim 12$$

$$BaCl_2 \downarrow \rightleftharpoons Ba^{2+} + 2Cl^- \quad . \quad . \quad . \quad . \quad - \ 0 \cdot 2$$

$$CdCl^+ \rightleftharpoons Cd^{2+} + Cl^- \quad . \quad . \quad . \quad . \quad - \ 0 \cdot 2$$

$$Br_3^- \rightleftharpoons Br_2 + Br^- \quad . \quad . \quad . \quad . \quad . \quad 1 \cdot 2$$

$$Br_5^- \rightleftharpoons Br_3^- + Br_2 \quad . \quad . \quad . \quad . \quad . \quad 0 \cdot 4$$

$$PbBr_2 \downarrow \rightleftharpoons PbBr^+ + Br^-; \quad pk_2 = 4 \cdot 1; \ pk_1 = 1 \cdot 1$$

$$TlBr \rightleftharpoons Tl^+ + Br^- \quad . \quad . \quad . \quad . \quad . \quad 5 \cdot 4$$

$$Ag_2Br_6^{4-} \rightleftharpoons AgBr \downarrow + Ag^+ + 5Br^- \quad . \quad - \ 2 \cdot 4$$

$$AgBr \downarrow \rightleftharpoons Ag^+ + Br^- \quad . \quad . \quad . \quad . \quad 12 \cdot 3$$

$$Hg_2Br_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2Br^- \quad . \quad . \quad . \quad . \quad 21 \cdot 3 \ (I = 0 \cdot 5)$$

$$AuBr_2^- \rightleftharpoons Au^+ + 2Br^- \quad . \quad . \quad . \quad . \quad 8$$

$$AuBr_4^- \rightleftharpoons Au^{3+} + 4Br^- \quad . \quad . \quad . \quad . \quad 25$$

$$CuBr_2^- \rightleftharpoons CuBr \downarrow + Br^-; \quad pk_2 = -2 \cdot 3; \ -3 \cdot 3; \ pk_1 = 8 \cdot 3$$

$$CuBr^+ \rightleftharpoons Cu^{2+} + Br^- \quad . \quad . \quad . \quad . \quad 0 \cdot 0$$

$$PtBr_4^{2-} \rightleftharpoons Pt^{4+} + 4Br^- \quad . \quad . \quad . \quad . \quad \sim 18$$

$$IBr_2^- \rightleftharpoons IBr + Br^- \quad . \quad . \quad . \quad . \quad . \quad 2 \cdot 6$$

$$I_2Br^- \rightleftharpoons I_2 + Br^- \quad . \quad . \quad . \quad . \quad . \quad 1 \cdot 2; \ 1 \cdot 1$$

$$I_3^- \rightleftharpoons I_2 + I^- \quad . \quad . \quad . \quad . \quad . \quad 2 \cdot 9$$

$$I_5^- \rightleftharpoons I_3^- + I_2 \quad . \quad . \quad . \quad . \quad . \quad 2 \cdot 5$$

$$PbI_4^{2-} \rightleftharpoons PbI_3^- + I^-; \quad pk_4 = 0 \cdot 5$$

$$PbI_3^- \rightleftharpoons Pb^{2+} + 3I^-; \quad pk_3 + pk_2 + pk_1 = 5 \cdot 4; \ 6 \cdot 3$$

$$PbI_2 \downarrow \rightleftharpoons PbI^+ + I^-; \quad pk_2 = 6 \cdot 4; \ pk_1 = 1 \cdot 5$$

$$TlI \downarrow \rightleftharpoons Tl^+ + I^- \quad . \quad . \quad . \quad . \quad . \quad 7 \cdot 2$$

$$HgI_4^{2-} \rightleftharpoons Hg^{2+} + 4I^- \quad . \quad . \quad . \quad . \quad 30; \ 31; \ 30 \cdot 3$$

$$HgI_2 \downarrow \rightleftharpoons Hg^{2+} + 2I^- \quad . \quad . \quad . \quad . \quad 25 \cdot 6; \ 28 \cdot 3$$

$$Hg_2I_2 \downarrow \rightleftharpoons Hg_2^{2+} + 2I^- \quad . \quad . \quad . \quad . \quad 28 \cdot 3; \ 27 \cdot 9$$

$$AuI \downarrow \rightleftharpoons Au^+ + I^- \quad . \quad . \quad . \quad . \quad . \quad 16$$

$$CuI_2^- \rightleftharpoons CuI \downarrow + I^- \quad . \quad . \quad . \quad . \quad 3 \cdot 1; \ 4 \cdot 0$$

$$CuI \downarrow \rightleftharpoons Cu^+ + I^- \quad . \quad . \quad . \quad . \quad . \quad 12 \cdot 0$$

$$AgI_4^{3-} \rightleftharpoons AgI \downarrow + 3I^- \quad . \quad . \quad . \quad - \ 1 \cdot 6$$

$$AgI \downarrow \rightleftharpoons Ag^+ + I^- \quad . \quad . \quad . \quad . \quad . \quad 16 \cdot 05$$

$$CdI_4^{2-} \rightleftharpoons CdI_3^- + I^-; \quad pk_4 = 1 \cdot 5; \ 1 \cdot 6; \ pk_3 = 2 \cdot 1; \ 1 \cdot 2; \ 1 \cdot 3;$$
$$pk_2 = 0 \cdot 8; \ 1 \cdot 2; \ pk_1 = 2 \cdot 1; \ 1 \cdot 9; \ 2 \cdot 0$$

Redox

$$Cl_2 + 2e \rightleftharpoons 2Cl^-$$
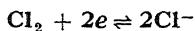
$E_0 = 1\cdot41$ volts for $\mid Cl_2 \mid = \mid Cl^- \mid^2$; $1\cdot36$ volts in solution saturated with chlorine for $\mid Cl^- \mid = 1$ (normal definition of potential in physical chemistry).

In HCl, $E = E_1 + 0\cdot03 \log \mid Cl_2 \mid$ with the following values of the formal potentials:

HCl	$0\cdot3N$	N	4N	6N	8N	12N
E(volts)	$1\cdot54$	$1\cdot39$	$1\cdot26$	$1\cdot21$	$1\cdot13$	$1\cdot04$

In $0\cdot2N$-H_2SO_4 $E = 1\cdot50$ volts.

$$Br_2 + 2e \rightleftharpoons 2Br^- \qquad E_0 = 1\cdot09 \text{ volts}$$
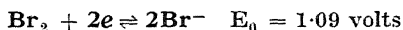
$E = 1\cdot09 + 0\cdot03 \log \mid Br_2 \mid$ volts for $\mid Br^- \mid = 1$.

In solution saturated with bromine, $1\cdot07$ volts for $\mid Br^- \mid = 1$.

In bromide solutions, bromine gives Br_3^-:

$$E = 1\cdot05 + 0\cdot03 \log \frac{\mid Br_3^- \mid}{\mid Br^- \mid} \text{ volts}$$

In chloride solution, Br_2Cl^- is formed, $E = 1\cdot13$ volts in N-HCl.

$$I_2 + 2e \rightleftharpoons 2I^- \qquad E_0 = 0\cdot62 \text{ volt (for } \mid I_2 \mid = \mid I^- \mid^2)$$
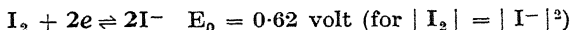
In solution saturated with iodine, $E = 0\cdot54$ volt for $\mid I^- \mid = 1$.

In the presence of Cl^-, Br^-, I^-, the complexes I_3^-, I_2Cl^- are formed and the potentials change slightly:

$$E = 0\cdot54 + 0\cdot03 \log \frac{\mid I_3^- \mid}{\mid I^- \mid^3} \text{ volt}$$

In HCl, we have for $\mid I_2 \text{ total} \mid = \mid I^- \text{ total} \mid$:

HCl	0	3N	6N	
E (volts)	$0\cdot65$	$0\cdot60$	$0\cdot52$	($0\cdot01M$–$0\cdot001M$ solutions)

The redox reactions are reversible with iodine; with bromine, oxidation of bromide is fairly slow; chlorides are not oxidized at a reasonable speed by any except the most powerful oxidants unless catalysts are present or the solution is heated.

The formal normal potential is independent of pH. As a result, even iodine becomes quite a strong oxidant in alkaline solution compared with the majority of other systems whose formal normal redox potentials in general decrease as the pH increases.

In alkalis, Cl_2, Br_2, and I_2 disproportionate.

In water, Cl_2 is in false equilibrium and should disproportionate so as to yield, finally, ClO_4^- and Cl^-. In practice, it first goes to HClO and Cl^-, a reaction which is practically quantitative at around pH 6. HClO is in false equilibrium but only disproportionates infinitely slowly in the cold.

Br_2 disproportionates at pH 7–8 into BrO^- and Br^-; BrO^- is in false equilibrium and goes very slowly over into BrO_3^- and Br^- in the cold. In the hot, BrO_3^- and Br^- are obtained as the final end products of the disproportionation of bromine, and this is nearly quantitative at about pH 8.

I_2 disproportionates giving first HIO and I^-, HIO is rapidly converted to IO_3^- and I^-; the transformation starts at about pH 9·5 and is complete at pH 11.

Cl_2/Cl^-: chlorides are oxidized in concentrated solution by MnO_4^-, IO_3^-, etc.

Chlorine is reduced by Br^-, I^-, $S_2O_3^{2-}$, and H_2S, the two last yield sulphates. NH_3 is oxidized to N_2. Organic dyestuffs are frequently destroyed.

$Br_2/2Br^-$: bromides are oxidized in acid solution by MnO_4^-, HClO, $Cr_2O_7^{2-}$, conc. sulphuric acid, and by PbO_2 even in acetic acid.

$I_3^-/3I^-$: iodides are oxidized by the oxidants just mentioned and by nitrous acid, ferric ions, arsenic acid in strong acid.

Iodine is reduced by hydrogen sulphide, with production of sulphur: in alkali, sulphides are oxidized to sulphates. Thiosulphates yield the tetrathionates in acid or neutral solution.

Detection of halides

Silver salts.—AgCl, AgBr, AgI have a low solubility in dilute nitric acid. AgCl is soluble in ammonia, AgBr is also soluble provided that an excess is added: the solubility of AgI in NH_3 is small, and it is bleached by this reagent. It is thus important, before carrying out any reaction, to find out whether Cl^-, Br^- and I^- are present or not by preliminary tests.

Interfering ions.—Black Ag_2S has a low solubility in $4N$-HNO_3; but oxidation dissolves it in the hot. H_2S can also be eliminated by acidifying and boiling before adding the Ag^+ ions. It can also be separated by means of cadmium acetate (see p. 289).

AgCNS is also of low solubility and dissolves in NH_3 to about the same extent as does AgBr. CNS^- can be destroyed by boiling in acid solution in the presence of HNO_2.

The white ferrocyanide and the orange ferricyanide are also of low solubility. They can be separated beforehand by means of Co^{2+}; to $\frac{1}{2}$ ml of solution add $\frac{1}{2}$ ml of 1–$2M$-H_2SO_4, and $\frac{1}{2}$ ml of 10 per cent cobalt acetate. Boil for a few minutes in the presence of paper pulp if necessary. Centrifuge.

CN^- which gives $Ag(Ag(CN)_2)$ gives the same reaction. Acidify with $HClO_4$ and heat in order to drive off the HCN before adding Ag^+. It is precipitated as $Co(CN)_2$ if Co^{2+} ions are added in excess.

$S_2O_3^{2-}$ gives a yellow precipitate of silver thiosulphate, which goes brown, then black as a result of conversion to silver sulphide. It can be eliminated by acidifying and boiling before adding Ag^+.

ClO^- interferes, since it gives ClO_3^- + AgCl, but when ClO^- is present Cl^- is also always present.

Reductants which reduce Ag^+, namely Fe^{2+}, Ti^{3+}, etc., should be oxidized beforehand by heating with HNO_3.

N_3^- interferes, and should be destroyed with HNO_2.

IO_3^- also precipitates as well as BrO_3^- and SO_4^{2-} in concentrated solution.

Detection of chlorides.—(1) **Oxidizing properties of chlorine.**— If a chloride be heated with an oxidant in excess, e.g. $KMnO_4$, in *dilute*

sulphuric acid, chlorine is liberated, whose oxidizing character can be demonstrated by a redox indicator, such as starch iodide paper, which goes blue, and then becomes colourless if excess of chlorine is present.

Interfering substances.—If Br^- and I^- are present, carry out the test as indicated later. NO_2^- and ClO^- can interfere. A mixture of *o*-toluidine and aniline can also be used to reveal the presence of free chlorine.

Solutions required

Saturated aqueous solution of aniline (3·5 per cent)			.	.	.	100 ml
,,	,,	,, ,, *o*-toluidine (1·5 per cent)			. .	20 ml
Acetic acid	. . . .					30 ml

Procedure.—A paper impregnated with this reagent mixture is used to reveal the presence of chlorine. A violet coloration is obtained.

Interfering substances.—I^-, CN^-, CNS^- are oxidized beforehand by HNO_2. Br^- interferes. See page 264 for the detection of Cl^- in the presence of Br^-.

(2) **Chromyl chloride.**—Powdered potassium dichromate liberates, on heating with a mixture of dried chloride and conc. sulphuric acid, brown vapours of chromyl chloride, CrO_2Cl_2. If the vapours are trapped in ammonia, the yellow chromate is obtained. Traces of chromate thus formed may be detected with diphenylcarbazide (see p. 172). The reaction can be carried out with the form of apparatus shown in fig. 92 (see p. 326).

Interfering substances.—The chlorides of silver and mercurous mercury whose solubility is low do not react. F^- and NO_3^- give a similar reaction. In addition, NO_3^- and also NO_2^- interfere, since they form $NOCl$. I^-, IO^-, IO_3^- give iodine and Br^-, BrO^-, and BrO_3^- give bromine. ClO_3^- and ClO_4^- are decomposed (danger of explosion) going partly to CrO_2Cl_2.

Detection of bromides.—(1) **Bromine.**—The oxidation of bromides in dilute solution of sulphuric acid or in acetic acid by solid potassium permanganate liberates bromine, and yields a brown solution in carbon tetrachloride. Its presence can also be revealed by redox indicators (starch iodide test paper, etc.), but this is less specific.

Interfering ions.—I_2, Cl_2, NO_2 are set free.

(2) **Formation of eosine.**—Free bromine reacts with fluorescein yielding tetrabromofluorescein, or eosine, a pink dye.

Material required.—A piece of pure filter paper (free from starch) is dipped in a saturated (5 per cent) alcoholic solution of fluorescein and then dried.

Procedure.—Bromine is liberated as indicated in (1). The slightly moist paper is held near the solution. A pink colour appears.

Interfering substances.—An excess of bromine decolorizes the paper but in that case the pink colour reappears on drying. Iodine from iodides gives a similar red stain. Iodides should therefore be separated beforehand, by means of nitrous acid, for example (see p. 264).

Much CN^- and CNS^- interfere. CN^- can be got rid of by

acidification and heating. Both these ions can be precipitated before-hand by adding Co(II) in excess (see p. 262).

BrO_3^- does not interfere if reductants are absent.

Concentration limit.—4.10^{-4} g.-ion/litre of Br^- (30 p.p.m.).

Detection of iodides.—(1) **Liberation of iodine.**—Nitrites in acid solution, $S_2O_8^{2-}$ in the cold, liberate iodine from iodides without oxidizing bromides and chlorides. Iodine gives violet vapours when heated and yields a violet solution in carbon tetrachloride.

Interfering substances.—CN^- interferes by giving ICN. It can be eliminated by acidification and heating.

If reductants are present, add an excess of HNO_2 to oxidize them.

Concentration limit.—10^{-5} g.-ion/litre in CCl_4. Below this it can still pro-duce a blue colour with starch paste. 5.10^{-6} g.-ion/litre of I^- (0·5 p.p.m.).

(2) **Starch paste.**—Iodine in presence of iodides gives adsorption compounds with certain substances when the latter are present in excess: blue adsorption compounds are produced by the amylose present in starch paste and soluble starch, and also by α-naphthoflavone. Glycogen gives a reddish-brown compound, etc. These colorations can be used to detect iodine: they disappear on heating and reappear on cooling.

The coloured compounds act as redox indicators. Below a potential of 0·60 volt they decolorize, since iodine is then absent. Between 0·60 and 0·90 volt the blue colour appears since both iodine and iodide are present. Above 0·90 volt the compound is decolorized, even in the presence of iodine, because iodide is absent. Above pH 9, the coloration diminishes in sensitivity because of the disappearance of iodine by disproportionation.

Detection of Cl^-, Br^-, I^- in a mixture.—(1) **Detection of I^-.**—Oxidize with HNO_2 or $S_2O_8^{2-}$ in acid solution, and extract the iodine liberated by means of CCl_4 (violet coloration).

(2) **Detection of Br^-.**—Treat the solution with PbO_2 in acetic acid or with dichromate in H_2SO_4 (1·5N): only bromine is liberated. It can be detected with eosine paper, starch iodide paper, or by extraction with CCl_4 (brown coloration).

The solution may also be diluted to pH 3–4, 0·2N permanganate added until the solution is pink and then extracted with CCl_4.

(3) **Detection of Cl^-.**—(*a*) Add excess solid permanganate, then *dilute* H_2SO_4 and then heat. Cl_2 is liberated, and its presence is revealed in the manner indicated above.

(*b*) The formation of chromyl chloride can also be used to reveal the presence of Cl^- in admixture with the other halide ions.

If the halide ions are present as a mixture of AgCl, AgI, AgBr, these latter can be reduced by adding 0·2 g of zinc powder and 1 ml of H_2SO_4 (1·5N); wait 10 minutes. Ag, Cl^-, Br^-, I^- are obtained.

The mixture of silver halides can also be fused with Na_2CO_3 in a loop of platinum wire; when the fused mass is taken up with water the same result is obtained.

Or the mixture can be boiled with sodium sulphide: Ag_2S and Cl^-, Br^-, I^- are obtained.

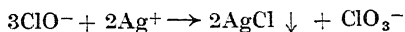## Oxidation State I+

Hypochlorites, Hypobromites, Hypoiodites

Influence of *p*H.—The hydroxides HClO, HBrO, and HIO, hypochlorous, hypobromous, and hypoiodous acids, are colourless and soluble.

$$Cl^+ \text{ very acid: } HClO \rightleftharpoons ClO^- + H^+; \quad pK = 7.3; \ 7.4$$
$$Br^+ \quad,, \quad ,, \ : HBrO \rightleftharpoons BrO^- + H^+; \quad pK = 8.7; \ 8.4$$
$$I^+, \ H_2O \rightleftharpoons IOH + H^+; \ pK = 4.5; \ HIO \rightleftharpoons IO^- + H^+; \ pK = 11 \text{ to } 12$$
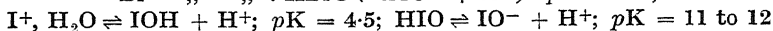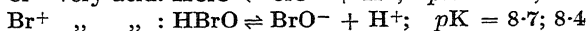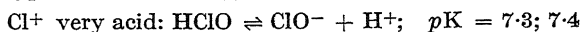
The acidity constants indicate the domains of existence of the different ions. All the compounds are in false equilibrium and should disproportionate; but the rate of transformation is slow with HClO, ClO⁻ and BrO⁻ in the cold; for I+, HIO, and IO⁻ it is rapid, the two latter however do exist for some time:

$$3IO^- \longrightarrow IO_3^- + 2I^-$$
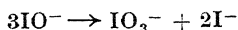
The disproportionation can be accelerated by the formation of low-solubility compounds:

$$3ClO^- + 2Ag^+ \longrightarrow 2AgCl \downarrow + ClO_3^-$$

Complexes.—Br(I) and I(I) exist in the form of yellow complexes: BrCl, ICl, ICl_2^-.

Low-solubility compounds.—AgIO and $Hg(IO)_2$ are known.
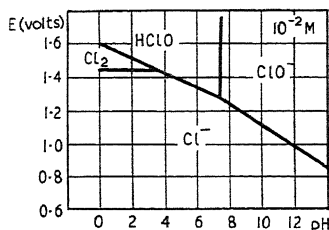
FIG. 78.—APPROXIMATE FORMAL POTENTIALS OF THE REDOX
SYSTEMS Cl(I)/Cl°/Cl⁻ AS A FUNCTION OF *p*H

Redox.—In the oxidation state I the three halogens are in unstable equilibrium in the range of *p*H covered by aqueous solutions. In actual fact these oxidation states for bromine and chlorine are only slowly disproportionated in the cold. Thus redox systems can be defined which permit the prediction of the reactions which actually occur.

They increase in oxidizing strength in going from iodine to chlorine, and are more oxidizing than the corresponding halogens in acid solution: the potential decreases when the *p*H increases.

$$2HClO + 2H^+ + 2e \rightleftharpoons Cl_2 + H_2O \quad E_0 = 1.63 \text{ volts}$$

(see fig. 78).

$$2HBrO + 2H^+ + 2e \rightleftharpoons Br_2 + H_2O$$
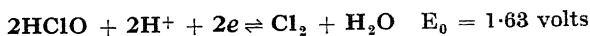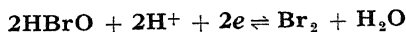
The calculated normal potential is 1.59 volts; 0.76 volt at *p*H 14 (fig. 79).
The calculated normal potential of the system HIO/I_2 would be 1.45.

But $I(I^+)$ is practically non-existent in solution. However, in solution sufficiently strong in HCl, we have

$$2ICl_2^- + 2e \rightleftharpoons I_2 + 4Cl^- \quad E_0 = 1 \cdot 00 \text{ volt}$$
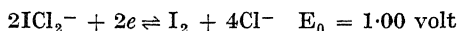
Disproportionation of ICl_2^- into IO_3^- and I_2 from pH 2.
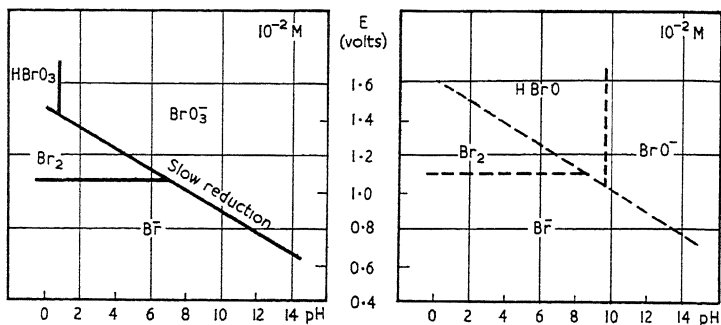
FIG. 79.—APPROXIMATE FORMAL POTENTIALS OF THE PRINCIPAL REDOX SYSTEMS OF BROMINE AS A FUNCTION OF pH

Formal normal potential is $0 \cdot 75$ volt in 6N-HCl.
In CN^- solution, we have

$$ICN + 2e \rightleftharpoons I^- + CN^- \quad E_0 = 0 \cdot 33 \text{ volt}$$

In very acid solution, HClO slowly oxidizes water:

$$2HClO \longrightarrow Cl_2 + 2H^+ + \tfrac{1}{2}O_2$$
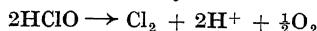
and HCl more rapidly:

$$HClO + Cl^- + H^+ \rightleftharpoons Cl_2 + H_2O$$
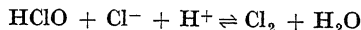
In alkali, the decomposition of ClO^- (involving the oxidation of water) is rapid in the hot in the presence of oxides of nickel and cobalt (see p. 195).

HClO and ClO^- oxidize I^- to IO_4^- and so do HBrO and BrO^-.

In alkali, hypochlorites and hypobromites are still strongly oxidizing. Their action on redox indicators can be deduced from the table on
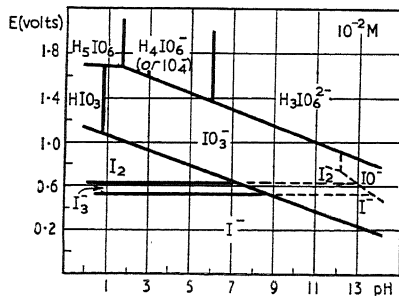
FIG. 80.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF IODINE AS A FUNCTION OF pH
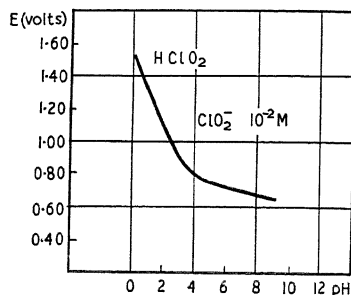
FIG. 81.—FORMAL POTENTIAL OF Cl(III) AS A FUNCTION OF pH

page 119. Dyes are generally destroyed. Thus indigo carmine (0·1 per cent) is decolorized in water by ClO^- when the solution is saturated with $NaHCO_3$.

The hypochlorites are reduced by hydrogen peroxide.

$HAsO_2$ reduces them in acid solution.

All these reactions, as well as their other oxidizing properties in weak acid, neutral, or alkaline solution, distinguish them from the chlorates.

Oxidation State III+

Chlorites

Cl^{3+}, a strong acid, does not exist. Chlorous acid, $HClO_2$, is colourless, $pK = 2·3$. The solubility of the yellow $AgClO_2$ is low.

$$HClO_2 + 3H^+ + 4e \rightleftharpoons Cl^- + 2H_2O$$
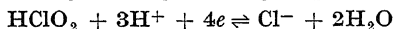
The formal potential is shown in fig. 81. Very slow from right to left, and from left to right above pH 5.

$HClO_2$ is in false equilibrium; it should finally disproportionate into ClO_4^- and Cl^- but this reaction is infinitely slow. In very strong acid, $HClO_2$ is not stable, it yields ClO_2 and ClO_3^-.

Iodine is oxidized at pH 4:

$$5HClO_2 + 2I_2 + 2H_2O \longrightarrow 4IO_3^- + 5Cl^- + 9H^+$$
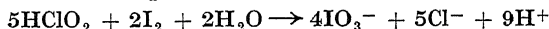
$HBrO_2$.—Bromous acid.

I(III).—HIO_2 forms as an intermediate in the disproportionation of iodine:

$$I_2 + OH^- \rightleftharpoons HIO + I^-; \quad 2HIO + OH^- \longrightarrow HIO_2 + I^- + H_2O$$

The reaction $HIO + HIO_2 \longrightarrow H_2I_2O_3$ (condensed compound corresponding to II+) also occurs.

HIO_2 is unstable and IO_3^- is finally obtained:

$$3IO_2^- \longrightarrow 2IO_3^- + I^-$$
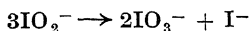
In HCl, ICl_3 and ICl_4^- are formed:

$$\frac{|\ ICl\ |.|\ Cl_2\ |}{|\ ICl_3\ |} = 7.10^{-4}$$
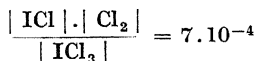
IBr_3 also exists.

Oxidation State V+

Chlorates, Bromates, Iodates

The cations do not exist. The complex corresponding to ICl_5 does exist, however, in very strong HCl.

$HClO_3$ is a strong acid, stronger than HCl; $HBrO_3$, $pK = 0·7$; HIO_3, $pK = 0·8$.

Anions and cations are colourless. No stable complexes.

Cl(V).—The chlorates are all soluble. The least soluble are: $KClO_3$ 0·6M, $AgClO_3$ 0·6M, $Ba(ClO_3)_2$ 0·9M.

In strongly acid and dehydrating solution (H_2SO_4) ClO_2 is formed, a yellow explosive vapour.

Br(V).—The solubility of many of the bromates is low: a few unstable complexes are known.

Equilibrium constants

$$KBrO_3 \downarrow \rightleftharpoons K^+ + BrO_3^- \quad \text{. . . . .} \quad 1\cdot 2$$
$$Pb(BrO_3)_2 \downarrow \rightleftharpoons Pb^{2+} + 2BrO_3^- \quad \text{. . . . .} \quad 1\cdot 7$$
$$TlBrO_3) \downarrow \rightleftharpoons Tl^+ + BrO_3^- \quad \text{. . . . .} \quad 3\cdot 4$$
$$Ba(BrO_3)_2 \downarrow \rightleftharpoons Ba^{2+} + 2BrO_3^- \quad \text{. . . . .} \quad 5\cdot 3$$
$$AgBrO_3 \downarrow \rightleftharpoons Ag^+ + BrO_3^- \quad \text{. . . . .} \quad 4\cdot 3$$
$$Th(BrO_3)_2{}^{2+} \rightleftharpoons ThBrO_3{}^{3+} + BrO_3^-; \quad pk_2 = 0\cdot 1; \; pk_1 = 0\cdot 8 \; (I = 0\cdot 5)$$

I(V).—HIO_3 is a colourless solid. I_2O_5 is a solid. Iodic acid is soluble to the extent of $0\cdot 5$M. $pk = 0\cdot 8$.

Equilibrium constants

$$Zn(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Zn^{2+} \quad \text{. . . . .} \quad 5\cdot 4$$
$$La(IO_3)_3 \downarrow \rightleftharpoons 3IO_3^- + La^{3+} \quad \text{. . . . .} \quad 9\cdot 2$$
$$Ca(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Ca^{2+} \quad \text{. . . . .} \quad 5\cdot 7$$
$$In(IO_3)_3 \downarrow \rightleftharpoons 3IO_3^- + In^{3+} \quad \text{. . . . .} \quad 10\cdot 6$$
$$Cu(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Cu^{2+} \quad \text{. . . . .} \quad 6\cdot 9; \; 7\cdot 1$$
$$Ba(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Ba^{2+} \quad \text{. . . . .} \quad 8\cdot 9$$
$$Sr(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Sr^{2+} \quad \text{. . . . .} \quad 9\cdot 6$$
$$TlIO_3 \downarrow \rightleftharpoons IO_3^- + Tl^+ \quad \text{. . . . .} \quad 5\cdot 3$$
$$Pb(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Pb^{2+} \quad \text{. . . . .} \quad 12\cdot 5$$
$$AgIO_3 \downarrow \rightleftharpoons IO_3^- + Ag^+ \quad \text{. . . . .} \quad 7\cdot 3$$
$$Hg(IO_3)_2 \downarrow \rightleftharpoons 2IO_3^- + Hg^{2+} \quad \text{. . . . .} \quad 18\cdot 7$$
$$Cd(IO_3)_2 \rightleftharpoons Cd^{2+} + 2IO_3^- \quad \text{. . . . .} \quad 7\cdot 65$$
$$Zn(IO_3)_2 \rightleftharpoons Zn^{2+} + 2IO_3^- \quad \text{. . . . .} \quad 5\cdot 4$$
$$Mn(IO_3)_2 \rightleftharpoons Mn^{2+} + 2IO_3^- \quad \text{. . . . .} \quad 6\cdot 3$$
$$Th(IO_3)_3{}^+ \rightleftharpoons Th(IO_3)_2{}^{2+} + IO_3^-; \quad pk_3 = 2\cdot 35; \; pk_2 = 1\cdot 9;$$
$$pk_1 = 2\cdot 9 \; (I = 0\cdot 5)$$

Addition of strong acids exerts fairly little effect on the solubility of iodates.

Redox.—ClO_3^- is in unstable equilibrium. It should disproportionate into ClO_4^- and Cl^-, but the reaction is infinitely slow in aqueous solution.

$$ClO_3^- + 6H^+ + 5e \rightleftharpoons \tfrac{1}{2}Cl_2 \uparrow + 3H_2O \quad E_0 = 1\cdot 47 \text{ volts (calculated)}$$
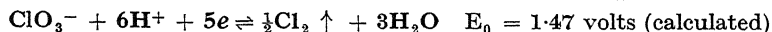
This value calculated from the equilibrium constants has scarcely any practical significance, because equilibrium is only established extremely slowly. In general the chlorates react at a practically zero rate, except in very acid solution.

The reduction potential at pH 0 is of the order of $0\cdot 1$ volt. In weak acid or neutral solution, osmic acid catalyses the reaction. The chlorates are not reducible in alkaline solution, even electrolytically.

In strong acid, chlorates are reduced by sulphurous acid, nitrous acid, Fe^{2+}, and conc. HCl.
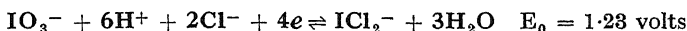
$$BrO_3^- + 6H^+ + 5e \rightleftharpoons \tfrac{1}{2}Br_2 \uparrow + 3H_2O \quad E_0 = 1\cdot 48 \text{ volts}$$
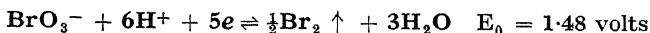
At pH < 3 bromates oxidize the bromides, iodides, etc. Above pH 3, they generally react very slowly.

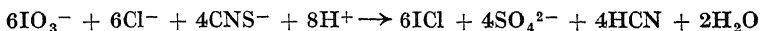$$IO_3^- + 6H^+ + 5e \rightleftharpoons \tfrac{1}{2}I_2 \downarrow + 3H_2O \quad E_0 = 1\cdot 19 \text{ volts}$$
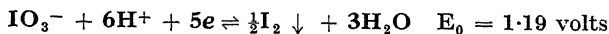
At pH > 5, iodates react very slowly. They oxidize concentrated hydrochloric acid.

In very strong HCl, the system:

$$IO_3^- + 6H^+ + 2Cl^- + 4e \rightleftharpoons ICl_2^- + 3H_2O \quad E_0 = 1 \cdot 23 \text{ volts}$$

is set up. Thus, in fairly conc. HCl, reactions of the following kind occur:

$$6IO_3^- + 6Cl^- + 4CNS^- + 8H^+ \dashrightarrow 6ICl + 4SO_4^{2-} + 4HCN + 2H_2O$$

Sulphurous acid reduces them to I^0, then to I^-. The reaction stops at the I^0 stage in very acid solution with Fe^{2+} and CNS^-.

Detection of bromates.—(Odekerken).—BrO_3^- is reduced to bromine which is detected with fluorescein, which gives a pink coloration due to the formation of eosine.

Solution required.—Saturated solution in 50 per cent alcohol of fluorescein, N/10 in NaOH.

Procedure.—To a drop of the solution, add several drops of the reagent and a crystal of ferrous sulphate.

Concentration limit.—$5 \cdot 10^{-4}$ BrO_3^- per litre (100 p.p.m.).

Interfering substances.—IO_3 and CNS^- give red colorations with Fe(III) and S^{2-} a black one. They should be precipitated with lead acetate. $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ give blue colorations. They should be separated with Cd acetate.

Detection of iodates.—(Odekerken).—It is reduced to iodine by CNS^- in acid solution. The iodine is detected as already indicated (p. 264).

Solution required.—1 per cent KCNS.

Procedure.—To 2 drops of the solution add a drop of N-HCl, a few drops of CCl_4 and a drop of thiocyanate. Shake. A violet coloration appears.

Concentration limit.—10^{-6} g.-ion/litre of IO_3^- (20 p.p.m.).

Detection of chlorates.—(1) **Reduction.**—Separate all the anions which can be precipitated as silver salts and centrifuge them out. To 2 drops of the filtered solution add 4N-HNO$_3$, then M-NaNO$_2$; ClO_3^- is reduced. AgCl precipitates.

Concentration limit.—$5 \cdot 10^{-4}$ g.-ion of ClO_3^- per litre (40 p.p.m.).

Interfering substances.—ClO_4^- is not reduced, and so does not interfere. HClO interferes; it is reduced by $HAsO_2$ in hot acid solution before precipitating with Ag^+; otherwise it would give chlorate by disproportionation during this precipitation.

A little BrO_3^- can escape precipitation and can then interfere.

(2) **Redox indicators.**—ClO_3^- oxidizes at an appreciable rate in strong acid. The table of redox indicators shows that diphenylamine is oxidized to a blue compound by a certain number of oxidants among which are the chlorates. The same reaction is given by BrO_3^-, IO_3^-, ClO^-, NO_3^-, $Cr_2O_7^{2-}$, IO_4^-, H_3AsO_4, etc. Note the difference from ClO_4^- which does not oxidize.

Solution required.—0·5 g of diphenylamine in 100 ml of conc. H_2SO_4.

Procedure.—To 2 drops of reagent, add 1 drop of the solution being examined.

Methyl orange in hot 6N-HCl is decolorized.

Benzidine and *o*-tolidine in 4–6N-HCl turn orange.

Concentration limit.—10^{-3} to 10^{-4} g.-ion of ClO_3^- per litre (10–100 p.p.m.).

Interfering substances.—The same as those mentioned above under *reduction,* except for H_3AsO_4, $Cr_2O_7^{2-}$ and NO_3^- which only interfere when present in very high concentration.

Reductants which do not react with chlorates in neutral or alkaline solution can reduce them in acid solution and can then inhibit all these reactions.

Oxidation State VII+

Perchlorates. Periodates

Cl(VII).—$HClO_4$ is the strongest acid known.

Only the perchlorates of potassium, caesium, ammonium and rubidium have a low solubility: $0.14M$-$KClO_4$ per litre. $KClO_4$ resembles $KMnO_4$ in properties.

Redox.—The rate of oxidation by dilute $HClO_4$ is extremely small, and only becomes at all marked with extremely powerful reductants. ClO_4^- can be reduced by zinc in acids, in the presence of green Mo(III) acting as a catalyst. Very energetic reductants such as hydrosulphites, Ti(III), $Fe(OH)_2$, reduce the perchlorate ion extremely slowly, even in the hot. It can be reduced by V(II), Cr(II), and the reduction is catalysed by I⁻, Mo(III), V(III), Re(V).

In hot concentrated $HClO_4$, or in the presence of catalysts, the speed of reaction is considerable. Seventy per cent acid is used as an oxidant at its b.p. of 200°. In more concentrated solution, the reduction can be so fast as to be explosive. I⁻, which catalyses reductions, is oxidized at as low a temperature as 135° to iodine; at 200° it is oxidized to HIO_3.

$$ClO_4^- + 2H^+ + 2e \rightleftharpoons ClO_3^- + H_2O \quad E_0 = 1.19 \text{ volt (calculated)}$$
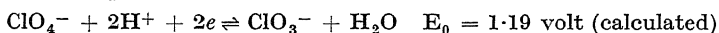
Br(VII).—Does not exist in any form in aqueous solution.

I(VII).—Solid HIO_4 and H_5IO_6 are known. The ions $H_6IO_6^-$ or IO_4^- and $H_3IO_6^{2-}$ or $I_2O_9^{2-}$ also exist.

Equilibrium constants

$$
\begin{array}{llll}
H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ & \quad . \quad . \quad . \quad . & 1.7;\ 3.3 \\
H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O & \quad . \quad . \quad . \quad . & -1.6 \\
H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ & \quad . \quad . \quad . \quad . & 8.4;\ 6.7 \\
H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ & \quad . \quad . \quad . \quad . & 15.0 \\
(NH_4)IO_4 \rightleftharpoons NH_4^+ + IO_4^- & \quad . \quad . \quad . \quad . & 1.8
\end{array}
$$
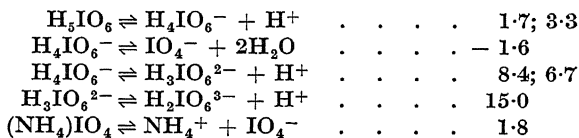
Numerous periodates are of low solubility.

Silver periodate $Ag_2H_3IO_6$ is blackish brown, undoubtedly due to the presence of AgO. $Ba_5(IO_6)_2$ or $Ba_2I_2O_9$, of low solubility in water, is soluble in concentrated acids. There are also periodates corresponding to H_3IO_5 and $H_8I_2O_{11}$.

$$H_5IO_6 + H^+ + 2e \rightleftharpoons IO_3^- + 3H_2O \quad E_0 = 1.7 \text{ volt (calculated)}$$
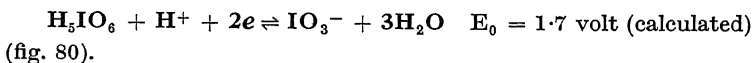
(fig. 80).

Periodates are strongly oxidizing, but react slowly. They oxidize manganous salts to permanganates in hot acid solution. They remain powerful oxidants in alkaline solution (fig. 80). Reduction above pH 5 generally halts at the IO_3^- stage, this then being reduced further slowly. H_2O_2 yields IO_3^- in neutral, acid, or alkaline solution. In acid solution,

Cl^- also yields iodate. The majority of sufficiently powerful reductants reduce periodates right to I^-. The reverse reaction is very slow in acids, but more rapid in alkalis. Thus hypochlorites oxidize iodates to periodates in alkali.

Detection of perchlorates.—(1) **Reduction.**—Precipitate with an excess of silver nitrate and in the presence of $HAsO_2$ if hypochlorites are present (see p. 269). Reduce the chlorates as mentioned on page 269. The solution resulting from the detection of chlorates is rendered alkaline, filtered, manganese nitrate added to it, evaporated to dryness, and ignited. Perchlorates are easily decomposed in the presence of the MnO_2 which is formed. Take up in water, acidify with HNO_3, and detect the Cl^- formed with Ag^+.

(2) **Precipitation of $KClO_4$.**—This test is not very sensitive, because $KClO_4$ is fairly soluble; it is also non-specific; ReO_4^-, SiF_6^{2-}, BF_4^-, AlF_6^{3-}, etc., also precipitate.

(3) **With methylene blue.**—This turns to violet in the presence of ClO_4^- on account of the precipitation of the perchlorate of the organic base. The reaction is rendered more sensitive by the presence of zinc salts.

Solution required.—50 per cent aqueous solution of $ZnSO_4.7H_2O$, 0·2 per cent solution of methylene blue in the above solution.

Procedure.—To a drop of solution, add $\frac{1}{2}$ ml of reagent. It turns violet in the presence of ClO_4^-.

Interfering substances.—$S_2O_8^{2-}$ gives the same reaction. Powerful oxidants destroy the dye.

Concentration limit.—10^{-3} g.-ion of ClO_4^- per litre (100 p.p.m.). 1 part of ClO_4^- can be detected in the presence of 1000 parts of ClO_3^-.

Detection of periodates.—(1) **Reduction and liberation of iodine.**—Numerous ions interfere.

(2) **Redox indicators.**—A certain number of indicators are oxidized, e.g. ferrous dimethylglyoxime in ammonia.

Interfering substances.—The same reaction is given by oxidants sufficiently powerful in alkaline solution: $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, ClO^-, MnO_4^-, BrO^-, I_2, H_2O_2.

CHAPTER X
HYDROGEN

$$H = 1 \cdot 008$$

States of oxidation.—I^- and I^+, the latter being the only important one. Detection of hydrogen is a part of gas analysis, and is simultaneous with its quantitative determination.

Solubility.—$0 \cdot 001M$ in water.

H(I⁻).—In certain hydrides, hydrogen is in the I^- oxidation state. Examples are: NaH, CaH_2. On the other hand, the hydrogen in the hydrides of the less electropositive elements is in the I^+ oxidation state: H_3As, H_2S. Arsine is thus really hydrogen arsenide, and *should* be formulated H_3As, the same being true for stibine, etc.

H^- is a very energetic base which reacts with H^+ liberating hydrogen:

$$H^- + H^+ \rightleftharpoons H_2 \uparrow \quad pK = 28 \text{ for } H_2 \text{ pressure of 1 atm.}$$
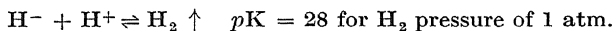
Thus
$$NaH \downarrow + H^+ \longrightarrow H_2 \uparrow + Na^+$$
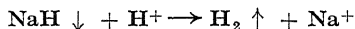
It is an energetic reductant which oxidizes itself to hydrogen:

$$2H^- - 2e \rightleftharpoons H_2 \uparrow \quad E_0 = -2 \cdot 2 \text{ volts for H pressure} = 1 \text{ atm.}$$
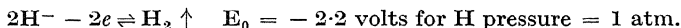
H(I⁺).—This is much the more important. Hydrogen ions H^+ are hydrated (see Chapter IV, Part I).

Complexes with H^+ are acids.

$$2H^+ + 2e \rightleftharpoons H_2 \uparrow \text{ (see p. 60)} \quad E_0 = -0 \cdot 06 \, pH \text{ for } H_2 \text{ pressure} = 1 \text{ atm.}$$
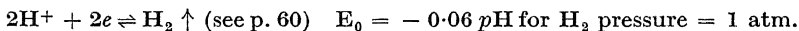
Hydrogen ions can act as oxidants, liberating hydrogen gas. The reaction is slow in both directions, as a result of which H ions are in general not in redox equilibrium with dissolved reductants. The reaction is catalysed by metals, particularly by finely divided Pt, Pd, etc. Very powerful reductants such as V(II) ($E_0 = -0 \cdot 20$ volt), Cr^{2+} ($E_0 = -0 \cdot 40$ volt) can reduce them, with liberation of hydrogen, in the presence of these catalysts. More energetic reductants do not exist in water owing to the presence of H^+.

Inversely, hydrogen can act as a reductant, but its action is very slow. The reaction can be catalysed, for example by metals with a large active surface: finely divided Pt, Pd, Ni. Palladous salts (PdII), silver oxide in the hot, I_2O_5, and picric acid are reduced by hydrogen.

The action of hydrogen on the oxidants like F_2, O_2 only takes place in the presence of traces of water:

$$\begin{array}{lll} O_2 \uparrow + 4H^+ + 4e \rightleftharpoons 2H_2O & \quad 1 \cdot 23 \text{ volts;} & -0 \cdot 06 \, pH \\ \underline{2H_2 \uparrow - 4e \rightleftharpoons 4H^+} & & \underline{-0 \cdot 06 \, pH} \\ O_2 \uparrow + 2H_2 \uparrow \rightleftharpoons 2H_2O \end{array}$$
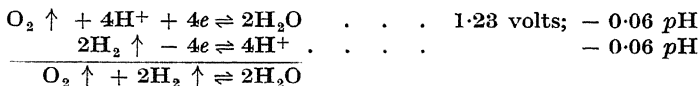
It is known that the last reaction does not occur unless substances which catalyse electron exchanges, e.g. finely divided platinum, are present, or at high temperatures at which the rates of reaction are very much increased.

IONS AND COMPOUNDS CONTAINING OXYGEN

OXYGEN

$$O = 16 \cdot 00$$

States of oxidation.—II⁻ and I⁻: these are the two most important. II⁺ is known in F_2O.

Oxygen

Solubility in water.—$1 \cdot 5 . 10^{-3}$ g.-mol/litre.

I⁻: Hydrogen peroxide. H_2O_2

For analytic purposes 20 vol. (6 per cent, $\sim 2M$) hydrogen peroxide is used, and also 'perhydrol' 100 vol. (30 per cent, $\sim 10M$).

Hydrogen peroxide is a slightly stronger acid than water.

Complexes and low-solubility compounds.—Hydrogen peroxide can donate H_2O_2, HO_2^-, O_2^{2-}, giving complexes. The stability of these complexes varies with the pH. They can also be destroyed by oxidation or reduction.

Low-solubility compounds with H_2O_2, HO_2^-, and O_2^{2-} can be obtained; their solubility varies with pH.

These complexes and low-solubility compounds are analogous to those obtained with H_2O, OH^-, O^{2-}. Thus, in the general case, we have cations in acid solution, similar to the basic ions of water, anions in alkaline solution, and compounds of low solubility which fall between the two. In general the compounds contain both water and hydrogen peroxide ions.

Thus Ti(IV) gives orange cations which can be $Ti(H_2O_2)^{4+}$, then TiO_2H^{3+}, TiO_2^{2+}, TiO_2OH^+. For example $TiO_2(OH)_2$ precipitates, which contains the ions Ti^{4+}, O_2^{2-}, $2O^{2-}$. Anions are formed in alkaline solution.

U(VI) gives an orange anion in alkaline solution, and a precipitate UO_4,aq. in neutral solution. It redissolves in very acid solution:

$$UO_4 \downarrow + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2$$
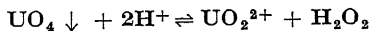
so that UO_4 contains U^{6+}, O_2^{2-}, $2O^{2-}$. No redox reactions are involved in any of these phenomena.

The compounds such as Na_2O_2, Li_2O_2 which are formed with the alkali metals are decomposed by water:

$$Na_2O_2 \downarrow + H_2O \rightarrow 2Na^+ + HO_2^- + OH^-$$
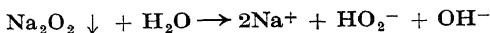
The compounds with the alkaline earths, BaO_2, etc., are soluble in acids. Numerous compounds are of low solubility in strong acid: Th_2O_7 or $2Th^{4+}$, $3O_2^{2-}$, O^{2-}.

The 'persalts' are soluble in water: $K_2C_2O_6$ or $2C^{4+}$, $2K^+$, $4O^{2-}$, O_2^{2-}, $NaBO_3$, $Na_2P_2O_8$.

Orange-coloured cations with Ti(IV), V(V), MO(VI), W(VI), U(VI), Nb(V) and blue ones with Cr(VI) are obtained.

Note.—Certain peroxides such as MnO_2, PbO_2 have different properties which can be explained in terms of Mn^{4+}, $2O^{2-}$, and Pb^{4+}, $2O^{2-}$. However, the two forms O^{2-} and $O_2{}^{2-}$ can in theory co-exist.

It has been proposed that the peroxides should be considered as compounds with hydrogen peroxide and the dioxides compounds with water, these latter corresponding to the metal in a higher oxidation state.

Equilibrium constants

$$H_2O_2 \rightleftharpoons HO_2{}^- + H^+ \quad . \quad . \quad . \quad pk_2 = 11\cdot7$$
$$HO_2{}^- \rightleftharpoons O_2{}^{2-} + H^+ \quad . \quad . \quad . \quad . \quad pk_1 = 25$$
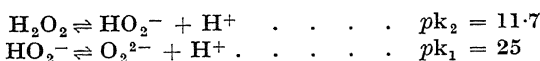
Note.—KO_2 contains $O_2{}^-$ (superoxide).
F_2O contains O^{2+}.

II^-: Water. H_2O

Water is a strongly ionizing liquid, and the equilibria studied in Chapter IV, Part I (p. 26), are set up in it. In particular:

$$OH^- \rightleftharpoons O^{2-} + H^+ \quad pK = 20\cdot8$$
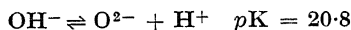
V	VI	VII
N(III-)	O(II-) S(II-)	F(I-)

O^{2-} is a strong base, stronger than F^- ($pK = 3\cdot2$), less basic than N^{3-} and slightly more basic than S^{2-} ($pK = 14\cdot9$).

Complexes.—These are anions and cations such as: $NO_3{}^-$, $AlO_2{}^-$, VO^{2+}, $Zr(OH)^{3+}$, etc. Their stability decreases in acid solution since O^{2-} is a base. A large number are perfect complexes (covalent): $NO_3{}^-$, $ClO_3{}^-$, $ClO_4{}^-$, $SO_4{}^{2-}$, etc.

Redox systems

We have in succession $O(II^-)$ in H_2O, $O(I^-)$ in H_2O_2, and $O(O)$ in O_2. Hydrogen peroxide only exists in metastable equilibrium and as a result the only stable system is H_2O/O_2.

$$(1) \quad 2O^{2-} - 4e \rightleftharpoons O_2 \quad \text{or} \quad 4OH^- - 4e \rightleftharpoons O_2 + 2H_2O$$

or $$2H_2O - 4e \rightleftharpoons O_2 + 4H^+$$
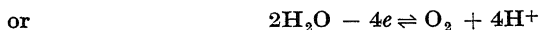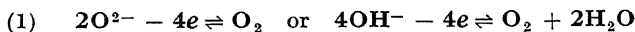
Water is the reductant, and O_2 the oxidant.

$$E = E_0 + \frac{0\cdot06}{4} \log \frac{|O_2| \cdot |H^+|^4}{|H_2O|^2}$$

or $$E = E_0 + \frac{0\cdot06}{4} \log \frac{|O_2|}{|O^{2-}|^2}$$

with $E_0 = 0\cdot26$ volt for $pK_1 = 10^{-20\cdot8}$.

For solutions in equilibrium with oxygen at atmospheric pressure, $E = 1\cdot23 - 0\cdot06\ pH$ or $E = 0\cdot22 - 0\cdot03 \log |O^{2-}|$ volt.

These are calculated values. The reaction rate is slow in both directions, as a result of which water is not in redox equilibrium with the majority of dissolved oxidants.

Oxygen very slowly oxidizes numerous systems in solution: ferrous ions, hydrogen sulphide, sulphites, etc. Strongly reducing systems are oxidized rapidly: $Fe(OH)_2$, $V(II)$, $Ti(III)$, etc. (see p. 60).

Water, OH^- and O^{2-} ions are oxidized even more slowly in general. Thus, strong oxidants like MnO_4^-, Ce^{4+} scarcely react at all; an additional potential difference is necessary. F_2 oxidizes water, Ag^{2+} does so slowly. The reaction is catalysed by finely divided platinum. The system CoO_2/Co_2O_3 (0·65 volt at pH 14) catalyses the oxidation of water (0·42 volt at pH 14) (see p. 195), e.g. by ClO^-.

In spite of the low rates of reaction, the O_2/H_2O system limits the existence of strongly oxidizing substances in water and that of strongly reducing substances in the presence of air.

(2) $$O_2 \uparrow - 2e \rightleftharpoons 2O^{2-}$$

or $$\boxed{H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O}$$
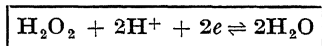
Hydrogen peroxide is the oxidant, water the reductant.

$$E = 1·77 + 0·03 \log | H_2O_2 | . | H^+ |^2 \text{ volts}; \quad E_0 = 0·89 \text{ volt at } pH \text{ 14}$$
$$\text{(calculated)}$$

or $$E = 0·82 + 0·03 \log \frac{| O_2^{2-} |}{| O^{2-} |^2} \text{ volt}$$

using the acidity constants on page 274.

Hydrogen peroxide in general oxidizes quite slowly, except systems already of fairly strong reducing strength: I^-, Fe^{2+}, N_2H_4, etc.

Catalysts: $Mo(VI)$ in neutral solution, $Os(VIII)$, etc.

Hydrogen peroxide also oxidizes in alkaline solution: CrO_2^- goes to CrO_4^{2-}, $Mn(OH)_2$ goes to MnO_2, etc.

Inversely, if it is desired to oxidize water to hydrogen peroxide, it is necessary to have a potential greater than 1·77 volts at pH 0, and very much above it if a reasonable rate of oxidation is desired. Under these conditions hydrogen peroxide is oxidized to oxygen more rapidly than it is formed, because a potential slightly above 0·68 volt is required for this. We then have the system H_2O/O_2.

(3) $$O_2^{2-} - 2e \rightleftharpoons O_2$$

or $$\boxed{H_2O_2 - 2e \rightleftharpoons O_2 + 2H^+}$$
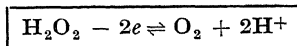
Oxygen is the oxidant, hydrogen peroxide the reductant.

$$E = 0·68 + 0·03 \log (| H^+ |^2/| H_2O_2 |) \text{ volt for } O_2 \text{ at 1 atm. pressure}$$

$$E_0 = -0·07 \text{ volt at } pH \text{ 14} \quad \text{or} \quad E = -0·38 + 0·03 \log | O_2 |/| O_2^{2-} | \text{ volt}$$

As a reductant, hydrogen peroxide in general reacts rapidly in acid solution, more slowly in alkaline solution.

Hydrogen peroxide reduces permanganate, hypochlorite, and ferricyanide in neutral or alkaline solution, PbO_2 in acid, iodate to iodine in acid solution, AgO in alkaline solution, auric salts, etc.

$$2Fe(CN)_6^{3-} + H_2O_2 \rightarrow 2Fe(CN)_6^{4-} + 2H^+ + O_2 \uparrow$$

$$2Au^{3+} + 3H_2O_2 \rightarrow 2Au \downarrow + 3O_2 \uparrow + 6H^+$$

19
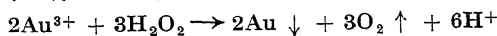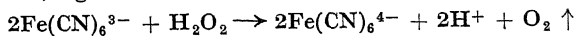
In the presence of cyanide, gold is oxidized thanks to the formation of a very stable aurocyanide complex:

$$2Au \downarrow + 4CN^- + H_2O_2 + 2H^+ \longrightarrow 2Au(CN)_2^- + 2H_2O$$
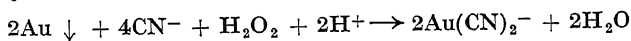
Inversely, to reduce oxygen to hydrogen peroxide, it suffices to have a potential lower than 0·68 volt. But then hydrogen peroxide can be reduced to water quite fast ($E_0 = 1·77$; considerable overvoltage).

Disproportionation.—Hydrogen peroxide is in metastable equilibrium, since, according to the potential values, a molecule of H_2O_2 acting as oxidant ought to react with another molecule of H_2O_2 acting as a reductant.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \uparrow \quad \text{or} \quad 2O_2{}^{2-} \longrightarrow 2O^{2-} + O_2 \uparrow$$
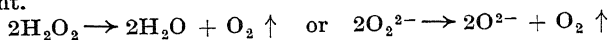
In equilibrium, the two potentials should be equal.

$$1·77 + 0·03 \log | H_2O_2 | . | H^+ |^2 = 0·68 + 0·03 \log \frac{| H^+ |^2}{| H_2O_2 |} \text{ (volt)}$$

whence:
$$\frac{1·09}{0·03} = \log \frac{1}{| H_2O_2 |^2} \quad \text{or} \quad | H_2O_2 | = 10^{-18}$$

The value of $| H_2O_2 |$ is thus extremely small, in fact practically negligible, in equilibrium. But since the reaction is so extremely slow, the disproportionation takes place only extremely slowly, and metastable solutions of hydrogen peroxide can be preserved for a very long time (so long as catalysts which can accelerate it are excluded).

Hydrogen peroxide disproportionates more rapidly in the presence of numerous catalysts such as MnO_2/MnO in neutral solution, CoO_2/Co_2O_3, finely divided platinum, etc. Raising the temperature accelerates the reaction. Stabilizers inhibit the decomposition: urea, acetanilide, disodium phosphate, etc. In acid solution, as we have seen, the rate of reaction is lower.

Catalysts of the system: $2H_2O - 4e \rightleftharpoons 4H^+ + O_2 \uparrow$
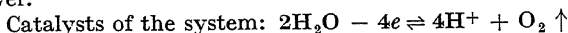
also catalyse the decomposition of hydrogen peroxide by reducing it:

whence
$$\frac{2H_2O_2 + 4H^+ + 4e \longrightarrow \quad 4H_2O}{2H_2O_2 \longrightarrow 2H_2O + O_2 \uparrow}$$
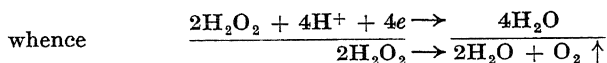
Hydrogen peroxide can be prepared at ordinary temperatures by the formation of compounds (complexes or of low solubility) which displace the disproportionation equilibrium in the direction

$$O_2 \uparrow + 2O^{2-} \longrightarrow O_2{}^{2-}$$
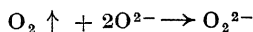
Detection of oxygen.—(1) Oxidation with change of colour of $Fe(OH)_2$, $Mn(OH)_2$ into rust-coloured $Fe(OH)_3$ and brownish-black $Mn(OH)_4$.

(2) Pyrogallol in alkaline solution absorbs oxygen and becomes deep brown in the process. The test-tube is inverted over a basin of mercury.

(3) A certain number of redox indicators can be used. Thus the leuco-derivative of methylene blue is reoxidized, going blue: $E = 0·00$ volt at pH 7. The leuco-derivative of indigo carmine can also be used.

Numerous oxidants give the same reaction.

Detection of water.—(A) **In a solid.**—Heat in test-tube previously baked out. The presence of droplets of water can be made more obvious by using some powdered potassium permanganate, which turns red.

(B) **In a liquid.**—Sodium liberates hydrogen slowly. Calcium carbide gives off acetylene. Carry out the test in test-tube inverted over a container of mercury. Wait several hours. *Concentration limit:* 5.10^{-3} of H_2O per litre.

(C) **In a liquid or solid.**—Distil in the presence of anhydrous benzene, toluene, or xylene. The first portion comes over cloudy in the presence of water as a result of the distillation of an azeotrope containing water. On cooling, water separates.

Detection of hydrogen peroxide.—(1) **Reduction of MnO_4^-,** causing its decoloration. Other reductants give the same reaction.

(2) **Reaction with titanium salts.**—Ti(IV) salts give in sulphuric acid (1·5N) an orange coloration due to the formation of a complex with O_2^{2-} (see p. 177).

Interfering ions.—Those which complex Ti(IV) strongly, such as F^- (see Ti(IV), p. 176).

(3) **Redox indicators.**—The detection of hydrogen peroxide can be effected by means of redox indicators, in the absence of other oxidants. Starch iodide turns blue. Some organic dyes change colours.

Ozone. O_3

A gas with a characteristic odour. Solubility 0·02M.

Redox

$$O_3 \uparrow + 2H^+ + 2e \rightleftharpoons O_2 \uparrow + H_2O \quad E_0(\text{calc.}) \sim 2 \cdot 0 \text{ volts}$$
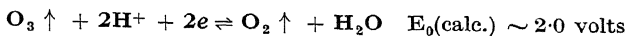
The potential in solution saturated with oxygen containing 10 per cent ozone at atmospheric pressure is 1·7 volts at pH 0.

But, in general, the reaction from left to right is slow, and the reverse reaction is very slow.

In addition, ozone slowly oxidizes water:

$$2O_3 \uparrow + 4H^+ + 4e \longrightarrow 2O_2 \uparrow + 2H_2O$$
$$\underline{2H_2O - 4e \longrightarrow O_2 \uparrow + 4H^+}$$
$$2O_3 \uparrow \longrightarrow 3O_2 \uparrow$$
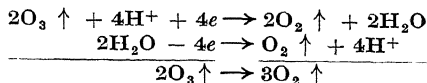
doing so more rapidly in alkaline solution.

It reacts with redox indicators: starch iodide is initially coloured blue (the same happens with Cl_2, H_2O_2, NO_2). With benzidine a brown compound is obtained. Ozone oxidizes the leuco-base of fluorescein, regenerating the original dye. Fluorescein itself is gradually destroyed. Organic dyes like indigo are decolorized. Lead sulphide is oxidized to sulphate.

Inversely, powerful oxidants oxidize water, giving ozonized oxygen: Ag^{2+}, F_2, etc.
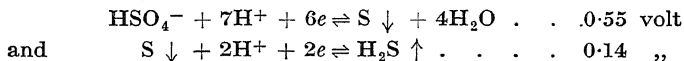
IONS AND COMPOUNDS DERIVED
FROM SULPHUR

$$S = 32\cdot06$$

THE principal states of oxidation and the corresponding calculated potentials, in so far as they are known, are given below (Latimer).

According to these values, a considerable number of compounds should vanish by disproportionation between pH 0 and pH 14. Thus $S_2O_6^{2-}$, H_2SO_3, $HS_2O_4^-$, $S_4O_6^{2-}$, $HS_2O_3^-$, scarcely exist at pH 0. $S_2O_8^{2-}$ is also present in aqueous solution in false equilibrium and should oxidize water. If equilibria were achieved, only HSO_4^-, S $\downarrow$, and H_2S should be present in aqueous solution at pH 0.

$$HSO_4^- + 7H^+ + 6e \rightleftharpoons S \downarrow + 4H_2O \quad . \quad .0\cdot55 \text{ volt}$$

and
$$S \downarrow + 2H^+ + 2e \rightleftharpoons H_2S \uparrow . \quad . \quad . \quad . \quad 0\cdot14 \text{ ,,}$$

However, the preceding compounds which only disproportionate very slowly ($HS_2O_4^-$ does so fairly fast) are found in false equilibrium, and also other condensed ions such as S_m^{2-}, $S_mO_6^{2-}$, etc.

We shall give the observed formal potentials as a function of pH for the various systems and the disproportionations which take place at a notable speed. We shall restrict ourselves to those systems which are of analytic interest.

V	VI	VII
	O	
P	S	Cl
	Se	
	Te	

S(II$^-$) SULPHIDES

The state of oxidation II$^-$ puts sulphur into the VI column of the periodic table. Its properties, very similar to those of selenium and tellurium, also resemble those of oxygen. The following equilibria occur:

$H_2O \rightleftharpoons OH^- + H^+$
$pk_2 = 15\cdot7$
$OH^- \rightleftharpoons O^{2-} + H^+$
$pk_1 = 20\cdot8$

$H_2S \rightleftharpoons HS^- + H^+$
$pk_2 = 7\cdot1$
$HS^- \rightleftharpoons S^{2-} + H^+$
$pk_1 = 14\cdot9, 12\cdot4,$
$11\cdot9, 13\cdot1$

$H_2Se \rightleftharpoons HSe^- + H^+$
$pk_2 = 3\cdot8$
$HSe^- \rightleftharpoons Se^{2+} + H^+$
$pk_1 = 11$
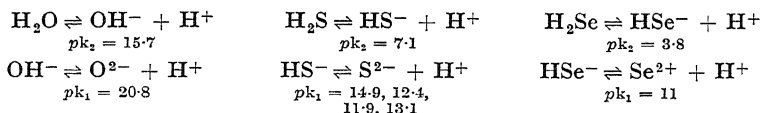
State of oxidation	Ions	Redox systems at pH 0
S(VIII)/S(VII) .	Caro's acid	$2SO_5^{2-} + 4H^+ + 2e \rightleftharpoons S_2O_8^{2-} + 2H_2O$
S(VII)/S(VI) .	Persulphate	$S_2O_8^{2-} + 2H^+ + 2e \rightleftharpoons 2HSO_4^-$
S(VI)/S(V) . .	Sulphate	$2HSO_4^- + 2H^+ + 2e \rightleftharpoons S_2O_6^{2-} + 2H_2O$
S(V)/S(IV) . .	Dithionate	$S_2O_6^{2-} + 4H^+ + 2e \rightleftharpoons 2H_2SO_3$
S(IV)/S(III) .	Sulphite	$2H_2SO_3 + H^+ + 2e \rightleftharpoons HS_2O_4^- + 2H_2O$
S(III)/S(2·5) .	Hydrosulphite	$2HS_2O_4^- + 2H^+ + 2e \rightleftharpoons S_4O_6^{2-} + 2H_2O$
S(2·5)/S(II) .	Tetrathionate	$S_4O_6^{2-} + 2H^+ + 2e \rightleftharpoons 2HS_2O_3^-$
S(II)/S(O) . . .	Thiosulphate	$HS_2O_3^- + 5H^+ + 4e \rightleftharpoons 2S \downarrow + 3H_2O$
S(O)/S(II$^-$) . .	Sulphide	$S \downarrow + 2H^+ + 2e \rightleftharpoons H_2S$

The second dissociation constant of H_2S indicates a fairly strong base.

H_2S is a gas whose solubility in water is 0·15 g.-mol/litre. It can be driven out of solution by boiling or by bubbling nitrogen, hydrogen, etc., through it. It is more soluble in acetone (0·65M). It has a characteristic odour and is toxic.

Solubility of the sulphides.—We have seen, page 80, how the apparent solubility of the sulphides varies as a function of the pH.

The differences of solubility of the sulphides are utilized in the classical methods of analysis, to separate the elements into different groups (p. 84). The alkali and alkaline earth sulphides and those of the aluminium group are soluble, those of the zinc group are soluble at pH 1, and of low solubility at pH 9. The sulphides of the arsenic and the mercury group are of low solubility at pH 1. Those of the arsenic group, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2, GeS_2, V_2S_5, MoS_3, WS_3, are soluble in an excess of sulphide as a result of the formation of sulphide complexes.

Notes.—(1) We have seen (p. 80) that the precipitation of sulphides is a little analogous to that of the hydroxides. It is frequently accompanied by complicated phenomena, formation of condensed ions; the colloidal form and later development of the precipitate is often considerable.

The phenomena can be formally represented by simple ions, to which solubility products can be ascribed.

(2) Basic sulphides can be formed, and also sulphochlorides, etc., before the sulphide itself comes down: this happens with Hg^{2+}, Pb^{2+}, etc. The formation of colloids can impede the filtration of the sulphides. The values indicated can be modified by changes of temperature and addition or presence of salts.

The solubility of sulphides varies with the size and the perfection of the particles, sometimes within wide limits. We have indicated, every time that it is possible, the two limiting values.

Precipitation can be retarded by the formation of chloride, sulphate, etc., complexes.

Complexes.—The sulphides of arsenic, tin, antimony, germanium, vanadium, molybdenum, tungsten, give with S^{2-} complex anions which are destroyed in acid or even in weakly alkaline solution.

The most stable complexes are those of Ge(IV), destroyed only in very acid solution, then those of W(VI) and Mo(VI). Some are not very stable, like HgS_2^{2-}.

E_0 (calc.) volts	Redox systems at pH 14	E_0 (calc.) volts
+ 2·05	$2SO_5^{2-} + 2H_2O + 2e \rightleftharpoons S_2O_8^{2-} + 4OH^-$	+ 2·05
+ 0·20	$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+ 0·20
+ 0·20	$2SO_4^{2-} + 2H_2O + 2e \rightleftharpoons S_2O_6^{2-} + 4OH^-$	− 0·33
− 0·23	$S_2O_6^{2-} + 2e \rightleftharpoons 2SO_3^{2-}$	− 0·40
~2	$2SO_3^{2-} + 2H_2O + 2e \rightleftharpoons S_2O_4^{2-} + 4H_2O$	+ 2·02
~0·1	$2S_2O_4^{2-} + 2H_2O + 2e \rightleftharpoons S_4O_6^{2-} + 4OH^-$	+ 0·1
+ 0·50	$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	+ 0·50
+ 0·14	$S_2O_3^{2-} + 3H_2O + 4e \rightleftharpoons 2S\downarrow + 6OH^-$	− 0·51
	$S\downarrow + 2e \rightleftharpoons S^{2-}$	

Solubility products of sulphides

MnS pink	.	.	.	.	15·2; 14·9	SnS	.	.	.	.	28·1
MnS green	.	.	.	22·0	Fe$_2$S$_3$	.	.	.	.	88
FeS	.	.	.	.	.	18·4–21·6	Hg$_2$S	.	.	.	.	30–45
Tl$_2$S	.	.	.	.	.	22·3–23·9	CuS	.	.	.	.	44·1
NiS	.	.	.	.	.	20·5–27·7	Ag$_2$S	.	.	.	.	48·8; 51·2
CoS	.	.	.	.	.	22·2–26·7	Cu$_2$S	.	.	.	.	49·6
ZnS	.	.	.	.	.	22·9–25·2	HgS	.	.	.	.	53·5
CdS	.	.	.	.	.	27·2–28·4	PtS	.	.	.	.	~ 70
PbS	.	.	.	.	.	27·4–29	Bi$_2$S$_3$	.	.	.	.	71·8

$$Sb_2S_3 \downarrow + 2H_2O + 2H^+ \rightleftharpoons 2SbO^+ + 3H_2S \qquad . \quad . \quad 30$$
$$As_2S_3 \downarrow + 2H_2O + 2H^+ \rightleftharpoons 2AsO^+ + 3H_2S \qquad . \quad . \quad 22·7$$
$$HgS_2{}^{2-} \rightleftharpoons Hg^{2+} + 2S^{2-}. \quad . \quad . \quad 54·7$$
$$AgHS \rightleftharpoons AgS^- + H^+ \quad . \quad . \quad . \quad 5·3$$
$$AgHS + H^+ \rightleftharpoons Ag^+ + H_2S \quad . \quad . \quad . \quad 9·25$$
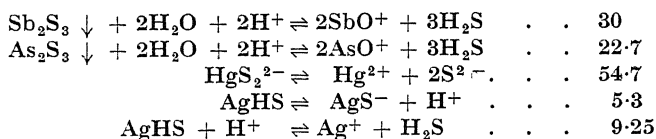
Notes.—In 9N-HCl at 100°, H$_2$S only precipitates As(III) and As(V).

In 9N-H$_2$SO$_4$ at 100°, As(III), Hg(II), Cu(II), Ag(I), Sb(III), Sb(V), Bi(III) precipitate.

In 3N-HCl at 100°, all those just mentioned come down except Bi(III).

In 0·3N-HCl at 100°, all those mentioned under H$_2$SO$_4$, and Sn(IV), Sn(II), Pb(II) and Cd(II) precipitate.

Redox

$$S^{2-} - 2e \rightleftharpoons S \downarrow \quad E_0 = -0·51$$

(the reaction from right to left is slow).

At *p*H 0, H$_2$S is very little ionized, and $E'_0 = 0·14$ volt (see fig. 82). Towards *p*H 12, S can disproportionate at a considerable

rate since then the sulphides can be directly oxidized to oxygenated sulphur compounds.
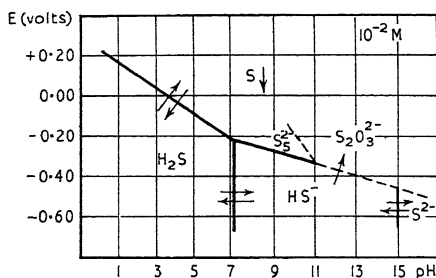
The solutions can be oxidized in the air. At *p*H < 11 (ammonium sulphide solution for example), orange polysulphides containing the ions S$_m{}^{2-}$ are formed, we then get oxygenated sulphur compounds. In more alkaline solution (sodium sulphide solutions, for example) there is direct oxidation to oxygenated sulphur compounds, and the solutions remain colourless.

The sulphides of low solubility are the less easily oxidized, the less soluble they are (see p. 99). In acid solution, iodine oxidizes them quantitatively to sulphur; the same is true of ferricyanides at *p*H 9. Powerful oxidants, MnO$_4{}^-$, Cl$_2$, Br$_2$, ClO$^-$, BrO$^-$, convert them to SO$_4{}^{2-}$.

Detection

(1) **Coloured sulphides.**—Addition of Ag^+ gives a black precipitate of Ag_2S whose solubility in 4N-HNO_3 is low. If the precipitate is boiled in this acid it is gradually oxidized to sulphate.

Other coloured sulphides can also be precipitated ($PbCO_3$ test paper, etc.).

Interfering substances.—AsH_3 and PH_3 do not precipitate Cd^{2+}, Zn^{2+}, Pb^{2+}, etc., but precipitate Ag^+. $S_2O_3^{2-}$ slowly precipitates Ag_2S in the cold.

(2) **Liberation of hydrogen sulphide.**—H_2S is liberated in acid solution. It can be detected by its odour or by its effect on a test paper.

Interfering substances.—Oxidants which do not react in alkaline solution, like the chlorates, can do so when the solution is made acid, and they then oxidize H_2S.

(3) **Oxidation of natural sulphides.**—Natural sulphides, little attacked sometimes by conc. HCl, can be oxidized by hot conc. HNO_3 which gives SO_4^{2-} and sometimes sulphur.

(4) **Alloys.**—When alloys are attacked by an acid, H_2S mixed with AsH_3 and PH_3 is liberated and is retained by zinc or cadmium acetate. CdS or ZnS alone precipitate.

Detection of traces.—**Nitroprusside.**—The ferrinitrocyanide or nitroprusside ion gives with S^{2-}, in alkaline solution, a violet coloration due to $[Fe(CN)_5(NO)S]^{4-}$.

Solution required.—1 per cent sodium nitroprusside.

Concentration limit.—6.10^{-4} g.-ion of S^{2-} per litre (20 p.p.m.).

Interfering substances.—Hardly any of the ions which can exist in the presence of sulphides interfere. SO_3^{2-} gives a slight pink coloration (see p. 286).

POLYSULPHIDES

They have the general formula S_m^{2-}, m having all values from 2 to 5; they are a more or less deep orange.

When acid is added, they are destroyed with precipitation of sulphur:

$$S_2^{2-} + H^+ \rightleftharpoons S\downarrow + HS^-$$
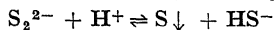
They are destroyed also by formation of low-solubility compounds:

$$S_2^{2-} + Zn^{2+} \rightleftharpoons S\downarrow + ZnS\downarrow$$
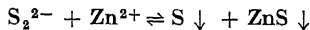
They are usually formed by dissolution of sulphur in the sulphides.

$2S^{2-} - 2e \rightleftharpoons S_2^{2-}$	$- 0.56$ volt
$3S_2^{2-} - 2e \rightleftharpoons 2S_3^{2-}$	$- 0.53$,,
$4S_3^{2-} - 2e \rightleftharpoons 3S_4^{2-}$	$- 0.48$,,
$5S_4^{2-} - 2e \rightleftharpoons 4S_5^{2-}$	$- 0.41$,,
$S_5^{2-} - 2e \rightleftharpoons 5S$	$- 0.43$,,

<div align="right">(G. VALENSI)</div>

S_5^{2-} can be obtained by oxidizing HS^- in not too alkaline solution (fig. 82) which itself can be oxidized to oxygenated sulphur compound.

SULPHUR

Detection.—(1) Heated on a piece of silver, it gives the black sulphide. Other sulphur compounds give the same reaction.

(2) Heating in alkaline solutions gives a sulphide whose presence can easily be detected (see above).

Disproportionation of sulphur takes place in very alkaline and hot solutions at a considerable rate; it partially stops at $S_2O_3^{2-}$:

$$4S \downarrow + 6OH^- \rightleftharpoons 2S^{2-} + S_2O_3^{2-} + 3H_2O$$
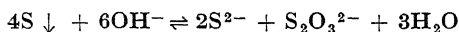
The sulphides formed can react with an excess of sulphur to give polysulphides $S_m{}^{2-}$.

Sulphides can be destroyed beforehand, if they are present, by boiling in acid solution. The solution and precipitate are then made alkaline with 4N-NaOH and then brought to the boil for a few minutes, in the presence of the solid under examination.

S(II⁺) THIOSULPHATES

Sulphur is in the II⁺ state of oxydation in sulphoxylic acid H_2SO_2, $pk_2 = 1.9$; $pk_1 = 7.0$. This is not very stable and is a strong reductant.

The condensed anion $S_2O_3^{2-}$ or thiosulphate corresponds to HSO_2^-.

Thiosulphuric acid is nearly as strong as sulphuric acid. It is thus stronger than sulphurous. Both the acid and the anion are colourless.

The silver salts blacken slowly in the cold and rapidly in the hot due to the formation of sulphide. This process is more rapid in acid solutions. The solubility of the barium salt is fairly low in water, 0·01M; it is more soluble in strong acid. The strontium salt is soluble, 0·9M, difference from sulphite. The solubility of the lead salt is low.

Complexes.—Thiosulphates give numerous complexes with Fe(III), Cr(III), Ag(I), Bi(III), Hg(II), Cu(II), Pb(II), Sb(III), As(III), etc.

In hot acid they are destroyed with precipitation of sulphur.

Equilibrium constants

$$H_2S_2O_3 \rightleftharpoons HS_2O_3^- + H^+ \quad \ldots \quad 0.3; 1.7$$
$$HS_2O_3^- \rightleftharpoons S_2O_3^{2-} + H^+ \ldots \quad 2.0; 2.5; 1.3$$
$$Ag(S_2O_3)_3{}^{5-} \rightleftharpoons Ag(S_2O_3)_2{}^{3-} + S_2O_3{}^{2-}; \quad pk_3 = -0.5 \text{ to } +0.4;$$
$$pk_2 = 0\text{--}0.4; \quad pk_1 = 13$$
$$Cd(S_2O_3)_4{}^{6-} \rightleftharpoons Cd(S_2O_3)_3{}^{4-} + S_2O_3{}^{2-}; \quad pk_4 \sim 1.1;$$
$$pk_3 + pk_2 + pk_1 = 6.3$$
$$FeS_2O_3 \rightleftharpoons Fe^{3+} + S_2O_3{}^{2-} \quad \ldots \quad 2.7$$
$$BaS_2O_3 \downarrow \rightleftharpoons Ba^{2+} + S_2O_3{}^{2-} \quad \ldots \quad 4.0$$
$$M_2{}^*(S_2O_3)_3 \downarrow \rightleftharpoons 2M^{3+} + 3S_2O_3{}^{2-} \ldots \quad 8.6\text{--}11.3$$
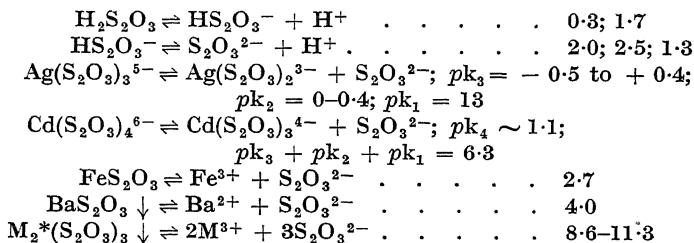
* M = Rare earth metal.

Redox.—(1) The thiosulphate ion is a reductant:

$$2S_2O_3{}^{2-} - 2e \rightleftharpoons S_4O_6{}^{2-} \text{ (tetrathionate ion)} \quad E = 0.1 \text{ volt (calculated)}$$
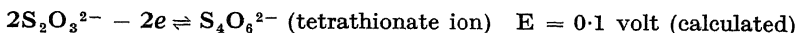
Electron exchange is in general very slow in the neighbourhood of this

potential. An oxidation potential can be defined above which $S_2O_3{}^{2-}$ reacts at a considerable speed in the majority of cases.

$$E = 0.21 - 0.06 \log | S_2O_3 |^{2-} \text{ volt}$$

(fig. 83).
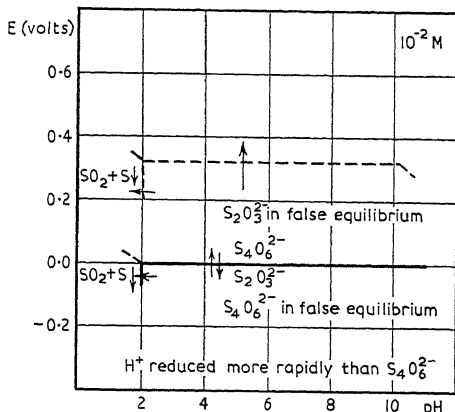
FIG. 83.—OXIDATION POTENTIALS OF $S_2O_3{}^{2-}$ AND REDOX POTENTIALS OF $S_2O_3{}^{2-}/S_4O_6{}^{2-}$

$S_4O_6{}^{2-}$ can practically not be reduced because H^+ is reduced more rapidly.

Oxidants such as iodine and ferric ions give tetrathionate quantitatively in neutral or weak acid solutions. Powerful oxidants give sulphate.

(2) **Thiosulphates can be reduced.**—In acid solution reduction takes place at the same time as disproportionation. Thus, with stannous chloride, tin sulphide and $S_2O_4{}^{2-}$ are obtained; with cuprous chloride, sulphur and cupric sulphide; with Mo(III) S, S^{2-}, $S_4O_6{}^{2-}$ are obtained. With very powerful reductants (Al for example), H_2S is finally obtained.

Disproportionations.—$S_2O_3{}^{2-}$ is in false equilibrium, it should disproportionate. In practice the following disproportionations are observed.

(1) $$HS_2O_3{}^- + H^+ \rightleftharpoons SO_2 \uparrow + H_2O + S \downarrow$$
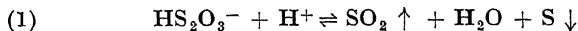
The equilibrium is displaced to the right in fairly acid solution, because of the formation and escape of sulphur dioxide.

In alkaline solutions on the other hand $S_2O_3{}^{2-}$ is obtained.

(2) $$S_2O_3{}^{2-} + H_2O \rightleftharpoons SO_4{}^{2-} + S^{2-} + 2H^+$$
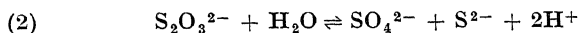
The disproportionation goes to the right with considerable speed only where very low solubility sulphides are formed (HgS, Ag$_2$S, etc.).

The overall redox systems are:

$$S_2O_3{}^{2-} + 6H^+ + 4e \rightleftharpoons 2S \downarrow + 3H_2O$$
$$2S_2O_3{}^{2-} + 4H^+ + 2e \rightleftharpoons S_2O_4{}^{2-} + 2S \downarrow + 2H_2O$$
$$S_2O_3{}^{2-} + 6H^+ + 6e \rightleftharpoons S_2{}^{2-} + 3H_2O$$
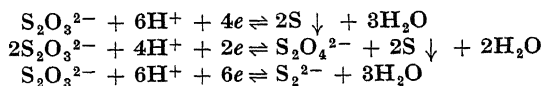
Detection.—Among the preceding properties the following can be utilized:

(1) **Silver salt.**—Add an excess of a silver salt to destroy the complex. $Ag_2S_2O_3$ precipitates. It goes yellow, and then black, slowly in the cold and rapidly on heating as a result of the formation of silver sulphide.

In the presence of cyanide only Ag_2S remains precipitated (Odekerken).

Solution required.—10 per cent silver nitrate.

Procedure.—To 0·5 ml of the solution add 1–2 ml of silver nitrate. Boil. Decant the solution. Add concentrated cyanide.

Concentration limit.—10^{-4} g.-ion/litre of $S_2O_3{}^{2-}$ (10 p.p.m.).

Interfering substances.—S^{2-}, $S_m{}^{2-}$ also give Ag_2S. They should be separated beforehand with cadmium acetate.

(2) **Action of acids.**—Liberation of sulphur dioxide which can be detected as indicated on page 286, and sulphur is precipitated.

Interfering substances.—S^{2-}, $S_m{}^{2-}$, $SO_3{}^{2-}$ (see p. 289). Numerous oxidants in acid solution.

S(III) HYDROSULPHITES

Hydrosulphurous acid, $H_2S_2O_4$ (also sometimes called hyposulphurous acid), is strong in its first dissociation; for the other dissociation, $pk_1 = 2·45$. It is of low stability, as is $S_2O_4{}^{2-}$, in aqueous solution. Disproportionation occurs.

Redox

$$HS_2O_4{}^- + 2H_2O \rightleftharpoons 2H_2SO_3 + H^+ + 2e \quad E_0 = -0·23 \text{ volt (calc.)}$$
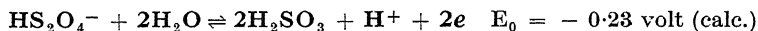
Formal potential $+ 0·07$ volt at pH 0.

$$S_2O_4{}^{2-} + 4OH^- \rightleftharpoons 2SO_3{}^{2-} + 2H_2O + 2e \quad . \quad . \quad -1·13 \text{ volts}$$
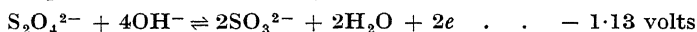
Sulphites can be reduced to hydrosulphites, but as the latter are of low stability, they disproportionate:

$$2S_2O_4{}^{2-} + H_2O \rightleftharpoons S\downarrow + 3SO_3{}^{2-} + 2H^+$$

$$3S_2O_4{}^{2-} + 3H_2O \rightleftharpoons S^{2-} + 5SO_3{}^{2-} + 6H^+ \text{ (see p. 286)}$$
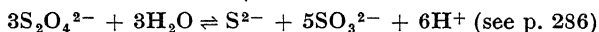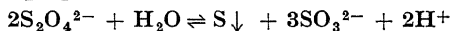
The hydrosulphites are obtained by reducing the bisulphites with Zn. Very strong reductants, they react with Ag and Cu salts yielding the metal. They reduce many redox indicators: indigo, methylene blue, oxidized ferrous dimethylglyoxime in ammonia.

S(IV) SULPHITES

S^{4+} is not known because it is too acid. SCl_4 and $SOCl_2$ are destroyed by water with formation of H_2SO_3.

SO_2 dissolves in water to the extent of $1·5M$ per litre and still more in alcohol. It is driven out of these solutions by boiling or by passing a current of gas through them.

The stability of H_2SO_3 is low:

$$H_2SO_3 \rightleftharpoons SO_2 \uparrow + H_2O$$

Its apparent acidity constants are: $pk_2 = 1·8$, $pk_1 = 5·3–7·1$. The acid and the anions are colourless.

The solubility of many sulphites in water is low, but they are soluble in acid. Ag_2SO_3, white, is soluble in weak acid solution. Barium sulphite, of low solubility in water, is soluble in acids; as a result of oxidation, $BaSO_4$ precipitates, difference from the carbonate. $SrSO_3$ is of low solubility, difference from the thiosulphate.

Complexes.—Some complexes, for example those with Ag^+, are destroyed by boiling, with precipitation of silver, as are those of the precious metals.

Equilibrium constants

$$H_2SO_3 \rightleftharpoons HSO_3^- + H^+; \ pk_2 = 1\cdot8; \ pk_1 = 5\cdot3\text{-}7\cdot1$$
$$CaSO_3 \downarrow \rightleftharpoons Ca^{2+} + SO_3^{2-} \quad . \quad . \quad . \quad . \quad . \quad 4\cdot0$$
$$Ag(SO_3)_2^{3-} \rightleftharpoons Ag^+ + 2SO_3^{2-} \quad . \quad . \quad . \quad . \quad . \quad 4\cdot3\text{-}8\cdot5$$
$$BaSO_3 \downarrow \rightleftharpoons Ba^{2+} + SO_3^{2-} \quad . \quad . \quad . \quad . \quad . \quad 8\cdot0$$
$$CeSO_3^+ \rightleftharpoons Ce^{3+} + SO_3^{2-} \quad . \quad . \quad . \quad . \quad . \quad 8\cdot0$$
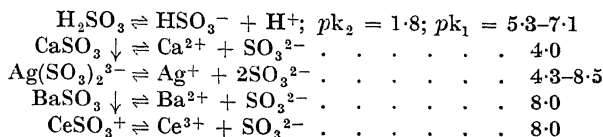
Redox.—(1) Sulphites are reductants.

$$2SO_3^{2-} - 2e \rightarrow S_2O_6^{2-} \quad \text{and} \quad SO_3^{2-} + H_2O - 2e \rightarrow SO_4^{2-} + 2H^+$$
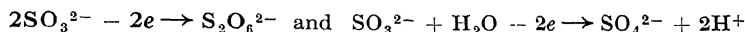
An oxidation potential for sulphite ion can be defined approximately, beyond which it is oxidized at a reasonable speed in the majority of cases.

$$E = 0\cdot33 - 0\cdot3 \log |SO_3^{2-}| \text{ volt (fig. 84)}$$

The normal potential calculated for a reversible system $H_2SO_3/S_2O_6^{2-}$ and also that of H_2SO_3/SO_4^{2-} is $0\cdot20$ volt at pH 0.
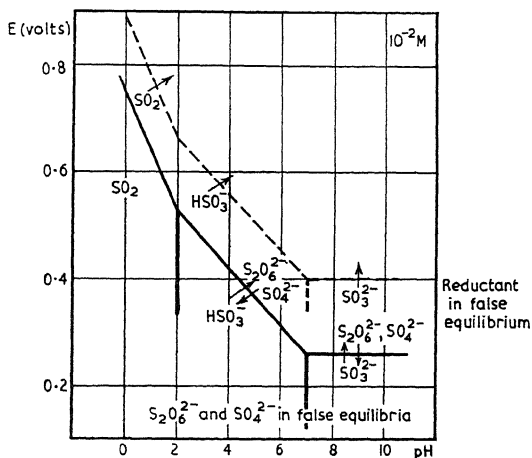
FIG. 84.—OXIDATION AND REDOX POTENTIALS OF SULPHITES

It is difficult to reduce the dithionates or the sulphites. Powerful oxidants give sulphate directly.

Sulphites in solution are oxidized by air. They reduce hydrogen peroxide, permanganate, starch iodide, $Cr_2O_7^{2-}$, etc. In general $S_2O_6^{2-}$ and SO_4^{2-} are formed. With MnO_2 in acid solution and IO_3^-, only $S_2O_6^{2-}$ can be obtained. The same occurs with Ag^+ and with $Fe(OH)_3$.

(2) **Sulphites can be reduced.**

$2H_2SO_3 + 2e + H^+ \rightleftharpoons HS_2O_4^- + 2H_2O$ (see p. 284) $E = -0.23$ volt
(calculated)
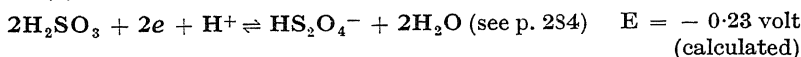
Measured potential $+ 0.07$ volt. At pH 14: -1.13 volt (calculated). $S_2O_4^{2-}$ forms and can disproportionate.

$$2S_2O_4^{2-} + H_2O \rightarrow S \downarrow + 3SO_3^{2-} + 2H^+$$
$$3S_2O_4^{2-} + 3H_2O \rightarrow S^{2-} + 5SO_3^{2-} + 6H^+$$
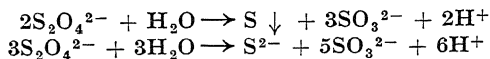
At pH 6, $S_2O_3^{2-}$ can be obtained. Whence the overall redox systems:

$$2SO_3^{2-} + 4H^+ + 2e \rightarrow S_2O_4^{2-} + 2H_2O$$
$$SO_3^{2-} + 6H^+ + 4e \rightarrow S \downarrow + 3H_2O$$
$$SO_3^{2-} + 6H^+ + 6e \rightarrow S^{2-} + 3H_2O$$
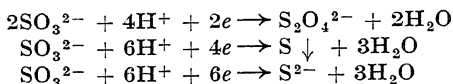
We then have as products of the reduction, according to the conditions (pH, low-solubility compounds), $S_2O_4^{2-}$, S and HS$^-$. The formation of low-solubility sulphites will favour the formation of HS$^-$. In concentrated HCl, Hg_2Cl_2, Fe^{2+}, CuCl reduce sulphurous acid to sulphur; Sn(II) reduces it to S^{2-}; Ti^{3+} reduces it to $H_2S_2O_4$ + S.

Disproportionation.—In the presence of platinum black as a catalyst, SO_3^{2-} disproportionates.

$3SO_3^{2-} + 2H^+ \rightarrow 2SO_4^{2-} + S \downarrow + H_2O$ and $4SO_3^{2-} \rightarrow 3SO_4^{2-} + S^{2-}$
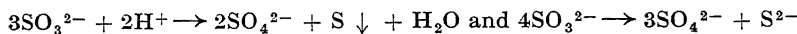
This shows very well, as do the calculated potentials (p. 279), that the sulphites are in false equilibrium.

<div align="center">

Detection

</div>

(1) **Action of acids.**—Acids give H_2SO_3 which decomposes with liberation of SO_2, which is driven out of solution in the hot. It can be detected by its odour or by its reducing properties (decoloration of MnO_4^-, of the blue adsorption compounds of iodine, etc.).

Interfering substances.—Oxidants which are frequently slow in action in alkaline can oxidize when the solution becomes acid and so inhibit the reaction. Thiosulphates also give sulphur dioxide.

(2) **Reducing properties.**—On MnO_4^- for example. The same substances interfere as previously, and also numerous reductants give the same reaction.

(3) **Formation of barium sulphate.**—Addition of hydrochloric acid and heating liberates sulphur dioxide which is trapped in acid barium chloride in the presence of hydrogen peroxide.

Interfering substances.—Under these conditions, carbonic acid does not interfere. Sulphides and thiosulphates also give a precipitate of barium sulphate.

Procedure.—The test is carried out by bringing the reagents: hydrogen peroxide, barium chloride, dilute hydrochloric acid, on the end of a stirring rod above the acidified solution and heating.

Concentration limit.—0.5–1 mg of SO_2.

(4) **Nitroprusside.**—Nitroprusside gives with sulphite a pink coloration more distinct in the presence of zinc sulphate.

Solutions required.—1 per cent sodium nitroprusside.

Saturated zinc sulphate solution.

Procedure.—To 2 drops of the solution add 2 drops of the zinc sulphate solution and then 1 of reagent.

Concentration limit.—10^{-3} g.-ion of SO_3^{2-} per litre (100 p.p.m.).

Interfering substances.—Sulphides should be eliminated by adding an excess of cadmium acetate and filtering.

Note.—This reaction is only of interest in the presence of thiosulphate.

Pyrosulphites and metabisulphites.—On heating, bisulphites lose the elements of water and give $M_2S_2O_5$, pyrosulphites or metabisulphites. But the condensed ions re-hydrate themselves rapidly in solution giving HSO_3^-.

S(VI) SULPHATES

Sulphuric acid is a strong acid in its first acidity. The second constant $pk_1 = 1\cdot9$ $(1\cdot0)$. The bisulphates, $KHSO_4$ for example, taken to dryness and gently ignited give the pyrosulphates such as $K_2S_2O_7$ which reproduce HSO_4^- in solution.

To the unknown cation S^{6+} correspond SO_2Cl_2, HSO_3Cl which are converted to SO_4^{2-} in water.

There is an azeotropic mixture of sulphuric acid and water containing 98·3 per cent of the former and boiling at 338°.

Low-solubility sulphates.—These are those of the alkaline earths, lead sulphate, certain anhydrous sulphates of chromium, ferric iron, as well as the basic sulphates of $Hg(II)$, $Bi(III)$, these latter being soluble in strong acids. The double sulphates of the alkalis and the ceric earths are of low solubility. Benzidine $(NH_2C_6H_4C_6H_4NH_2)$ sulphate has a low solubility. The sulphates are slightly more soluble in concentrated acids, since $pk_1 = 1\cdot9$.

Complexes.—Unstable ones with $Zr(IV)$, $Fe(III)$, $Mn(IV)$, $Sn(IV)$, etc. Very unstable ones with other cations.

Equilibrium constants

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \quad . \quad . \quad . \quad . \quad 1\cdot9\ (1\cdot0)$$
$$Ag_2SO_4 \downarrow \rightleftharpoons 2Ag^+ + SO_4^{2-} \quad . \quad . \quad . \quad 4\cdot2$$
$$CeSO_4^{2+} \rightleftharpoons Ce^{4+} + SO_4^{2-} \quad . \quad . \quad . \quad 3\cdot4$$
$$CaSO_4 \downarrow \rightleftharpoons Ca^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 4\cdot2$$
$$Hg_2SO_4 \downarrow \rightleftharpoons Hg_2^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 6\cdot3$$
$$SrSO_4 \downarrow \rightleftharpoons Sr^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 6\cdot6$$
$$PbSO_4 \downarrow \rightleftharpoons Pb^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 7\cdot7$$
$$BaSO_4 \downarrow \rightleftharpoons Ba^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 10\cdot0$$
$$Ba(HSO_4)_2 \rightleftharpoons Ba^{2+} + 2HSO_4^- \quad . \quad . \quad . \quad -0\cdot4$$
$$BaSO_4 \downarrow \rightleftharpoons Ra^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad 10\cdot4$$
$$Cu(SO_4)_3^{4-} \rightleftharpoons Cu^{2+} + 3SO_4^{2-} \quad . \quad . \quad . \quad -1\cdot8\ \text{to}\ -2\cdot3\ (I = 1)$$
$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-} \quad . \quad . \quad . \quad -1\cdot0\ (I = 1)$$

Redox.—(1) A certain number of sulphur compounds are oxidized to SO_4^{2-}; this is the case with SO_3^{2-} for example, which is oxidized to $S_2O_6^{2-}$ and SO_4^{2-}. But these systems are not reversible and SO_4^{2-} cannot

be reduced in dilute solutions in the cold. On the other hand, concentrated sulphuric acid can be reduced by I^- and in the hot by many metals: Cu, Ag, etc.

Metals can sometimes reduce it to the state of H_2S.

(2) Sulphates can be oxidized to persulphate, but only by electrolysis (see p. 289).

Detection

(1) **Barium sulphate.**—Low solubility in strong acids.

Solution required.—1 per cent barium chloride.

Procedure.—To 0·5 ml of solution, add 0·5 ml of 4N-HCl. If necessary centrifuge after bringing to the boil. To the clear solution add an equal volume of reagent. Barium sulphate precipitates, slowly in dilute solution.

Concentration limit.—10^{-4} g.-ion of SO_4^{2-} per litre (10 p.p.m.).

Interfering substances.—SeO_4^{2-} and SiF_6^{2-} give the same reaction. The first is reduced by hot concentrated HCl. The second is destroyed by boiling with ammonia. Polysulphides which would give a precipitate of sulphur should be separated with cadmium acetate, and thiosulphates destroyed in acid solution.

Note that in very strong HCl, $BaCl_2$ can precipitate; it redissolves on dilution.

Coloration by permanganate.—In the presence of potassium permanganate the latter is co-precipitated with barium sulphate and the precipitate is coloured pink. The subsequent addition of a reductant, for example H_2O_2 or HNO_2, decolorizes the solution by reduction of the permanganate, and does not decolorize the precipitate.

Procedure.—Acidify the solution with dilute HCl and heat to drive off volatile reductants; add several drops of 1 per cent MnO_4^-, then a drop of 5 per cent barium chloride. Then add H_2O_2 drop by drop until the red colour of the solution disappears. Observe the pink precipitate.

Interfering ions.—Substances which reduce permanganate, and in particular sulphur compounds. SiF_6^{2-} does not interfere because $BaSiF_6$ does not become coloured.

(2) **Detection in solids.**—(a) Heat a little of the powder in a small test-tube with a piece of magnesium ribbon to incandescence. Take up with a little water and detect the sulphide formed, for example, by the blackening of silver.

Fuse with alkali, take up with water and filter. Detect SO_4^{2-} in the solution.

In both these cases, numerous sulphur compounds interfere.

S(VII) PERSULPHATES

Persulphuric acid, $H_2S_2O_8$, is a strong acid in both its dissociations.

The solubility of potassium persulphate is low. Barium persulphate which is soluble gives the low-solubility sulphate on boiling. Silver persulphate appears to be soluble but the solution goes brown by formation of AgO.

Redox

$$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-} \quad E = 2 \cdot 05 \text{ volts}$$
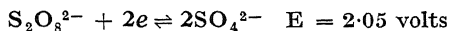
In the majority of oxidations by persulphate electron exchange is slow. In general it oxidizes compounds whose potential is below $\sim 1 \cdot 1$ volts, at a reasonable rate. However, Ag^+ is exceptional and is oxidized rapidly to $Ag(II)$ ($1 \cdot 98$ volts). In the presence of silver ions persulphates act fairly rapidly in strong acid. In this way $Mn(II)$ can be oxidized to $Mn(VII)$ in the hot, $Ce(III)$ to $Ce(IV)$ and Pb^{2+} to PbO_2. Ferrous *o*-phenanthroline is oxidized in the cold. NH_4^+ slowly gives N_2 and NO_3^-.

In alkaline solution persulphate oxidizes even in the absence of a catalyst. In neutral or acetic acid solution benzidine is oxidized to a blue compound (difference from compounds of oxygen, analogy with powerful oxidants). Solutions containing persulphate ions slowly liberate oxygen.

THIONATES

Under the term thionates are classed very varied condensed compounds whose general formula is $S_mO_6^{2-}$ where m varies from 2 to 6. The corresponding acids are fairly strong.

The more important thionate ions are:

(1) Dithionate $S_2O_6^{2-}$ ($S(V)$) is obtained by oxidation of sulphites. It is not oxidized by permanganate in alkali, which distinguishes it from the other thionates; however, in hot strong acid it disproportionates and can then be oxidized.

$$H_2S_2O_6 + H_2O \rightarrow SO_2 \uparrow + H_2O + HSO_4^- + H^+$$

(2) Tetrathionate $S_4O_6^{2-}$. This is obtained by oxidation of thiosulphates. It can be reduced with difficulty; for example, with sodium amalgam in the hot $S + SO_4^{2-} + SO_3^{2-}$ are obtained; with hydroxylamine in strong alkali, $S_2O_3^{2-}$ is obtained.

QUALITATIVE ANALYSES OF A MIXTURE OF SULPHIDE, SULPHITE AND THIOSULPHATE

(1) Detect the sulphide, then precipitate it by adding excess of cadmium acetate. Filter off the CdS. SO_3^{2-} and $S_2O_3^{2-}$ remain in solution.

(2) Buffer with acetate mixture and heat. Sulphurous acid is weak and unstable, sulphur dioxide comes off. Thiosulphuric acid is unstable but strong and, at pH $4 \cdot 5$, it remains mainly as the ions $S_2O_3^{2-}$. Then add $9N$-H_2SO_4, thiosulphuric acid is destroyed with liberation of sulphur dioxide and precipitation of sulphur.

(3) Sulphite and thiosulphate can also be separated by adding strontium chloride. Strontium sulphite precipitates, the thiosulphate is soluble. Heat and wait 2 hours before filtering off the $SrSO_3$.

(4) Sulphite and thiosulphate can be detected without separating them:
(*a*) sulphite by nitroprusside in the presence of zinc sulphate;
(*b*) thiosulphate by silver nitrate.

(5) $S_2O_3^{2-}$ and S^{2-} can also be separated by adding an excess of mercuric chloride. Wait a few minutes. Acidify. Detect the SO_2 which is liberated and which indicates the presence of sulphites.

SELENIUM AND TELLURIUM

$$Se = 79 \cdot 0; \; Te = 127 \cdot 6$$

V	VIb		VII	
		volts		volts
N	O . .	$0 \cdot 26$	F . . .	$+ 2 \cdot 8$
P	S . .	$- 0 \cdot 51$	Cl . . .	$+ 1 \cdot 4$
As	Se . .	$- 0 \cdot 77$	Br . .	$+ 1 \cdot 1$
Sb	Te . .	$- 0 \cdot 84$	I . . .	$+ 0 \cdot 6$
	Po			

THESE elements are neighbours of sulphur in virtue of their important states of oxidation: II^-, IV^+, VI^+.

II^-.—H_2O is a weak acid, $pk_2 = 15 \cdot 7$; $pk_1 \sim 21$. H_2S is less weak, $pk_2 = 7 \cdot 1$; $pk_1 \sim 15$.

H_2Se is still less weak: $pk_2 = 3 \cdot 7$; $pk_1 = 11$; 14.

H_2Te, $pk_2 = 2 \cdot 7$; $pk_1 = 10 \cdot 8$.

In column VIb of the periodic classification, the anions O^{2-}, S^{2-}, Se^{2-}, and Te^{2-} are less and less basic. H_2O, H_2S, H_2Se, H_2Te are more and more oxidizable.

The three hydrogen compounds are gaseous and can be oxidized in the air. The alkali and alkaline earths are soluble. Polysulphides, polyselenides, and polytellurides are red. The majority of metallic salts are of low solubility and analogous to the sulphides. Silver telluride is still less soluble than the sulphide.

Te_2^{2-} also occurs with the disproportionation:

$$Te_2^{2-} \rightleftharpoons Te \downarrow + Te^{2-}; \quad \frac{\mid Te^{2-} \mid}{\mid Te_2^{2-} \mid} = 10^{-2 \cdot 4}$$
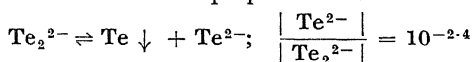
Elements.—The elements exist in many modifications. Selenium precipitates red in the cold; it becomes grey in the hot. The different species of tellurium are brown to black. There is a disproportionation in alkaline solutions as with sulphur.

IV^+.—H_2SO_3 is a weak acid: $pk_2 = 1 \cdot 8$; $pk_1 = 7 \cdot 1$.

H_2SeO_3, $pk_2 = 2 \cdot 6$; $pk_1 = 8 \cdot 3$.

H_2TeO_3, $pk_2 = 2 \cdot 7$; $pk_1 = 8$.

The solubility of tellurous acid is low. It precipitates in acetate buffer, and redissolves very little in strong acid, giving mainly $TeOOH^+$ and also Te^{4+}; $0 \cdot 01M$ in N-HCl and $HClO_4$. It is amphoteric and in alkaline solutions gives tellurites, TeO_3^{2-}. Basic salts can precipitate: TeO_2, HNO_3. There are also complexes such as $TeCl_6^{2-}$.

$$TeO_2 \downarrow + H_2O \rightleftharpoons HTeO_2^+ + OH^- \quad . \quad . \quad . \quad 16 \cdot 1$$
$$H_2TeO_3 \downarrow \rightleftharpoons HTeO_2^+ + OH^- \quad . \quad . \quad . \quad 11$$
$$3H_2O + TeO_3^{2-} \rightleftharpoons Te^{4+} + 6OH^- \quad . \quad . \quad . \quad 46$$
$$Te^{4+} + 2H_2O \rightleftharpoons HTeO_2^+ + 3H^+ \quad . \quad . \quad . \quad 0 \cdot 7$$
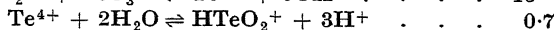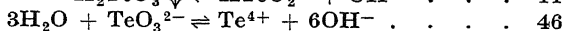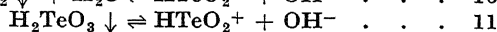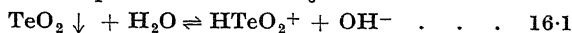
The majority of the salts are of low solubility but soluble in strong acid. $PbSeO_3$, 7·0; $BaSeO_3$, 7·0.

VI$^+$.—No cations.

H_2SO_4, strong in first dissociation, $pk_1 = 1·9$.

H_2SeO_4, first dissociation strong, $pk_1 = 1·8$.

For H_2TeO_4 it is reported that $pk_2 = 7·7$, 7·8, and $pk_1 = 11·2$, 10·3. However, corresponding to $Te(OH)_6$, $H_5TeO_6^-$, $H_2TeO_6^{4-}$, TeO_6^{6-} are known.

All the sulphates are soluble except those of barium, strontium and lead. The same is true of the selenates. $BaSeO_4$, 7·0; $SrSeO_4$, 5·0; $CaSeO_4$, 0·6; $AgCNSe$, 15·4.
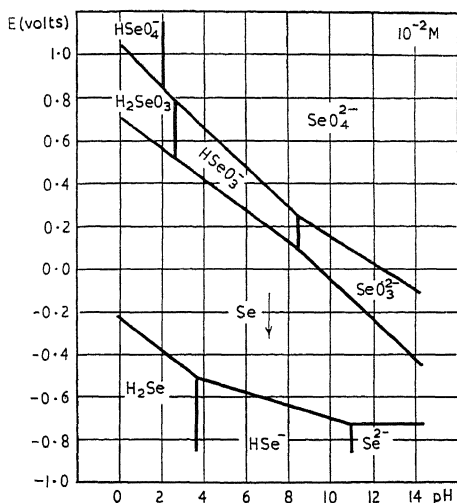
FIG. 85.—APPROXIMATE FORMAL NORMAL POTENTIALS OF THE REDOX SYSTEMS OF SELENIUM AS A FUNCTION OF pH

Redox

$$Se \downarrow + 2e \rightleftharpoons Se^{2-} \qquad -0·77 \text{ volt}$$
$$2Se \downarrow + 2e \rightleftharpoons Se_2^{2-} \qquad \sim -0·4 \text{ ,,}$$
$$Te \downarrow + 2e \rightleftharpoons Te^{2-} \qquad -0·92 \text{ ,,}$$
$$2Te \downarrow + 2e \rightleftharpoons Te_2^{2-} \qquad -0·84 \text{ ,,}$$
$$H_2SeO_3 + 4H^+ + 4e \rightleftharpoons Se \downarrow + 3H_2O \qquad 0·65 \text{ ,,}$$
$$Se^{4+} + 4e \rightleftharpoons Se \downarrow \qquad 0·74 \text{ ,,}$$
$$TeO_2 \downarrow + 4H^+ + 4e \rightleftharpoons Te \downarrow + 2H_2O \qquad 0·53 \text{ ,,}$$
$$HTeO_2^+ + 3H^+ + 4e \rightleftharpoons Te \downarrow + 2H_2O \qquad 0·56 \text{ ,,}$$
$$Te^{4+} + 4e \rightleftharpoons Te \downarrow \qquad 0·57 \text{ ,,}$$
$$TeCl_6^{2-} + 4e \rightleftharpoons Te \downarrow + 6Cl^- \qquad 0·55 \text{ ,,}$$
$$SeO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SeO_3 + H_2O \qquad 1·1 \text{ volts (calc.)}$$

$Te(OH)_6$ or H_2TeO_3 is of low solubility. In saturated solution in $9N$-H_2SO_4 $E = 0·57$ volt; $0·2N$-HNO_3, $E = 0·21$ volt; Te/TeO_3^{2-}, pH 14, $E = -0·12$ volt.

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Hydrogen sulphide, which produces sulphur slowly on reaction with sulphur dioxide, gives a yellow precipitate of selenium and sulphur with selenous acid and a brown precipitate in the case of tellurium. These precipitates are soluble in alkali sulphides. Hydrazine, hydroxylamine, phosphorous and hypophosphorous acids in the cold, and $Sn(II)$, reduce both selenous and tellurous acids to red selenium and black tellurium. Inversely, nitric acid and hot concentrated sulphuric acid oxidize selenium and tellurium.

SO_4^{2-}/SO_3^{2-} is not reversible. The same is true for selenium and tellurium. SO_4^{2-}, SeO_4^{2-}, and TeO_4^{2-} are difficult to reduce. Sulphuric acid cannot be reduced except when hot and concentrated. Selenic and telluric are not reduced except in very acid and hot solutions or by very powerful reductants; HCl hot and concentrated, $Ti(III)$.

Separation and characterization of selenium.—In sufficiently acid solution, e.g. 6N-HCl, sulphurous acid and iodides reduce selenous acid to red selenium. Black tellurium is precipitated by the same reductants, but only in weak acid. In the hot, SeO_4^{2-} is also reduced. Similarly, in sufficiently concentrated H_2SO_4, SO_2 reduces both SeO_4^{2-} and H_2SeO_3 in the hot.

Procedure.—To $\frac{1}{2}$ ml conc. H_2SO_4 add $\frac{1}{2}$ ml of the solution; saturate with SO_2. Boil for a minute. A red precipitate or coloration indicates the presence of selenium.

Concentration limit.—10^{-4} g.-ion/litre (10 p.p.m.).

IONS AND COMPOUNDS DERIVED FROM NITROGEN

NITROGEN

$$N = 14 \cdot 01$$

IV	V	VI
C	N	O
Si	P	S

IN the periodic classification nitrogen comes above phosphorus, to which it is similar, and between carbon and oxygen. The rules governing the strength of acids and bases in the classification apply here.

States of oxidation.—All values from III^- to V^+. The more important are III^-, III^+, V^+. The potentials calculated for the redox systems are as follows (Latimer):

		pH 0		pH 14
		volts		volts
$N(III^-)/N(II^-)$	NH_4^+—$N_2H_5^+$	1·22	NH_3—N_2H_4	+ 0·10
$N(II^-)/N(I^-)$.	$N_2H_5^+$—NH_3OH^+	1·48	N_2H_4—NH_2OH	+ 0·74
$N(I^-)/N(0)$.	NH_3OH^+—$N_2 \uparrow$	− 1·87	NH_2OH—N_2	− 3·04
$N(0)/N(I^+)$.	$N_2 \uparrow$—$H_2N_2O_2$	2·75	N_2—$N_2O_2^{2-}$	+ 1·60
$N(I^+)/N(II^+)$	$H_2N_2O_2$—$NO \uparrow$	0·60	$N_2O_2^{2-}$—$NO \uparrow$	+ 0·10
$N(II^+)/N(III^+)$	$NO \uparrow$—HNO_2	0·99	$NO \uparrow$—NO_2^-	− 0·46
$N(III^+)/N(IV^+)$	HNO_2—$N_2O_4 \uparrow$	1·07 ⎫	NO_2^-—NO_3^-	+ 0·01
$N(IV^+)/N(V^+)$.	$N_2O_4 \uparrow$—NO_3^-	0·81 ⎭		

According to the values of these potentials no compound between NO_3^{3-} and NH_4^{4+}, except nitrogen, should exist on account of disproportionations and we should have only the systems:

$$2NO_3^- + 12H^+ + 10e \rightleftharpoons N_2 \uparrow + 6H_2O \quad E_0 = 1 \cdot 22 \text{ volts}$$
and $\quad N_2 \uparrow + 8H^+ + 6e \rightleftharpoons 2HN_4^+ \quad E_0 = 0 \cdot 28 \text{ volt}$ ⎱ at pH 0
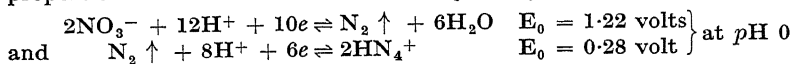
The intermediate compounds, however, all exist, evidently in false equilibrium. Nearly all react very slowly; only the potentials of the systems NO_3^-—HNO_2 and HNO_2—NO in acid solutions are of practical significance.

N(III⁻) AMMONIA

Ammonia is a colourless gas with a characteristic odour, very soluble in water. The concentrated solution, having a density 0·9, is 15M. Ammonia can be completely driven out of its solutions by boiling or by bubbling an inert gas through them.

NH_3 can play the part of a base, being stronger than PH_3 or H_2O.

$$NH_3 + H^+ \rightleftharpoons NH_4^+; \quad pK = 9 \cdot 2$$
$$NH_4OH \rightleftharpoons NH_3 + H_2O \quad . \quad . \quad . \quad . \quad 1 \cdot 4$$

293
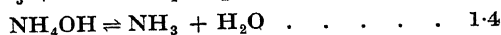
Numerous ammine complexes are formed with cations, see the table below; the majority are destroyed by acids. The cobaltiammines, more stable, are not destroyed.

NH_4^+ has been studied with the alkali metals.

NH_3 behaves as an acid in the nitrides such as AlN, Ca_3N_2 which are completely destroyed by the hydrogen ions of water.

$$N^{3-} + 3H^+ \longrightarrow NH_3$$

or $$Ca_3N_2 \downarrow + 6H^+ \longrightarrow 3Ca^{2+} + 2NH_3$$
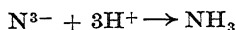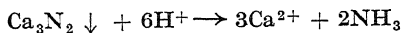
One acidity of NH_3 is neutralized in the amides which are destroyed by water.

$$NH_2^- + H^+ \longrightarrow NH_3$$

or $$NaNH_2 \downarrow + H^+ \longrightarrow NH_3 + Na^+$$

Equilibrium constants

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 9 \cdot 2$$

$Mg(NH_3)_6^{2+} \rightleftharpoons Mg(NH_3)_5^{2+} + NH_3$; $\quad pk_6 = -1 \cdot 3$; $pk_5 = -0 \cdot 95$;
$\qquad pk_4 = -0 \cdot 7$; $pk_3 = -0 \cdot 4$; $pk_2 = -0 \cdot 15$;
$\qquad pk_1 = 0 \cdot 2 \ (I = 2)$

$Cd(NH_3)_6^{2+} \rightleftharpoons Cd(NH_3)_5^{2+} + NH_3$; $\quad pk_6 = -1 \cdot 7$; $pk_5 = -0 \cdot 3$;
$\qquad pk_4 = 0 \cdot 9$; $pk_3 = 1 \cdot 4$; $pk_2 = 2 \cdot 1$; $pk_1 = 2 \cdot 6$

$Co(NH_3)_6^{2+} \rightleftharpoons Co(NH_3)_5^{2+} + NH_3$; $\quad pk_6 = -0 \cdot 6$; $pk_5 = 0 \cdot 2$;
$\qquad pk_4 = 0 \cdot 8$; $pk_3 = 1 \cdot 0$; $pk_2 = 1 \cdot 6$; $pk_1 = 2 \cdot 1$
$\qquad (I = 2)$

$Ni(NH_3)_6^{2+} \rightleftharpoons Ni(NH_3)_5^{2+} + NH_3$; $pk_6 = 0 \cdot 03$; $pk_5 = 0 \cdot 8$;
$\qquad pk_4 = 1 \cdot 2$; $pk_3 = 1 \cdot 7$; $pk_2 = 2 \cdot 2$; $pk_1 = 2 \cdot 8 \ (I = 2)$

$Cu(NH_3)_5^{2+} \rightleftharpoons Cu(NH_3)_4^{2+} + NH_3$; $\quad pk_5 = -0 \cdot 5$; $pk_4 = 2 \cdot 1$;
$\qquad pk_3 = 2 \cdot 9$; $pk_2 = 3 \cdot 5$; $pk_1 = 4 \cdot 15$

$Ag(NH_3)_2^+ \rightleftharpoons AgNH_3^+ + NH_3$; $\quad pk_2 = 3 \cdot 8$; $pk_1 = 3 \cdot 3$
$\qquad (I = 1 \text{ at } 30°)$

$Hg(NH_3)_4^{2+} \rightleftharpoons Hg(NH_3)_3^{2+} + NH_3$; $\quad pk_4 = 0 \cdot 8$; $pk_3 = 1 \cdot 0$;
$\qquad pk_2 \sim 8 \cdot 8$; $pk_1 \sim 8 \cdot 8$

$Cu(NH_3)_2^+ \rightleftharpoons CuNH_3^+ + NH_3$; $\quad pk_2 = 4 \cdot 9$; $pk_1 = 5 \cdot 9$

$Co(NH_3)_6^{3+} \rightleftharpoons Co(NH_3)_5^{3+} + NH_3$; $\quad pk_6 = 4 \cdot 4$; $pk_5 = 5 \cdot 0$; $pk_4 = 5 \cdot 6$;
$\qquad pk_3 = 6 \cdot 1$; $pk_2 = 6 \cdot 7$; $pk_1 = 7 \cdot 3 \ (I = 2)$

$Zn(NH_3)_4^{2+} \rightleftharpoons Zn(NH_3)_3^{2+} + NH_3$; $\quad pk_4 \approx pk_3 \approx pk_2 \approx pk_1 \approx 2$
$\qquad \text{at } 30°$

Low-solubility ammonium compounds, see p. 140.

Redox.—NH_3 can be irreversibly oxidized by powerful oxidants; the halogens and ClO^- and BrO^- oxidize NH_4^+ and NH_3 with liberation of nitrogen; $S_2O_8^{2-} + Ag^+$ do the same.

Inversely, nitrites and nitrates can be irreversibly reduced by powerful reductants to NH_4^+, or to NH_3 by $V(II)$ in acid or by zinc in alkali.

Ammonium, NH_4, which exists as an amalgam under high pressure is a very strong reductant:

$$NH_4 \downarrow - e \rightleftharpoons NH_4^+ \quad E \sim -1 \cdot 5 \text{ volts at } 100 \text{ atm.}$$
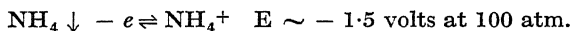
Detection of NH_3 and NH_4^+.—See page 140.

N(II⁻) HYDRAZINE NH₂—NH₂

This is a base.

$$NH_3^+NH_3^+ \rightleftharpoons NH_2NH_3^+ + H^+; \quad pk_2 = -0.3$$
$$NH_2NH_3^+ \rightleftharpoons NH_2NH_2 + H^+; \quad pk_1 = 7.9$$
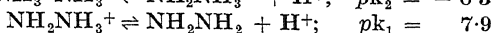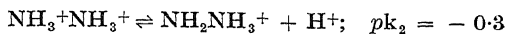
Redox.—All the redox reactions are slow. Hydrazine is a reductant and mainly produces nitrogen.

$$NH_2NH_3^+ - 4e \longrightarrow N_2 \uparrow + 5H^+ \quad E = -0.17 \text{ volt; at } pH\ 14 - 1.15 \text{ volts}$$
$$\text{(calculated)}$$
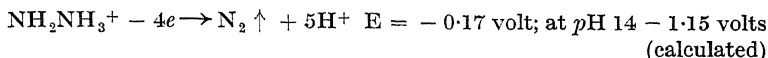
The formal oxidation potentials are: 0·1 in alkali of pH 8–12; about 0·6 volt at pH 0 and $-$ 0·4 volt at pH 14.

The reducing properties are weak in acid solution. However Au(III), MnO_4^- are reduced, V(V) gives V(IV). In alkali the reaction is more rapid. $Ag(NH_3)_2^+$, HgO, I_2 are reduced.

N(I⁻) HYDROXYLAMINE NH₂OH

This is a solid, melting at 33°, and is a base.

$$NH_2^+, H_2O \rightleftharpoons NH_2OH + H^+; \quad pk = 6$$
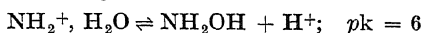
The basicity diminishes as the oxidation number increases from NH_3 through N_2H_4 to NH_2OH.

Redox.—All the reactions proceed irreversibly.

Hydroxylamine is a weak oxidant giving hydrazine and ammonia. It reduces slowly in acid solutions, more rapidly in alkali, giving nitrogen and nitrous and nitric oxides.

Formal oxidation potential: $\sim$ 0·7 volt at pH 0.

V(IV) reduces hydroxylamine in neutral solution giving NH_3, N_2, and NO; in alkali it gives NH_3. Cu_2O gives NH_3; and so does $Fe(OH)_2$.

V(V) and Fe^{3+} oxidize it in acid solutions.

HYDRAZOIC ACID HN₃

The salts are called azides (they should not be confused with the nitrides, p. 294).

The acid is a liquid boiling at 37°, soluble in water. The solution distils at a constant boiling point and fumes in the air. $pk = 4.7$.

The azides have properties similar to those of the halides. The salts of Cu^+, Pb^{2+}, Tl^+, Ag^+, Hg_2^{2+} are of low solubility. With ferric salts an intense red complex FeN_3^{2+} is formed.

Hydrazoic acid is toxic. The azides are detonable. Those of the heavy metals are particularly dangerous.

$$FeN_3^{2+} \rightleftharpoons Fe^{3+} + N_3^- \quad . \quad . \quad . \quad . \quad . \quad 4.3$$
$$AgN_3 \downarrow \rightleftharpoons Ag^+ + N_3^- \quad . \quad . \quad . \quad . \quad . \quad 8.6$$

Redox.—N_3^- is oxidized in acid solution giving nitrogen.

$$2N_3^- - 2e \longrightarrow 3N_2 \uparrow \quad E_0 = -3.2 \text{ volts (calculated)}$$

In practice, Ce^{4+}, MnO_4^- are decolorized in the hot whilst Cr(VI) is not reduced. The reaction is slow. However, nitrous acid oxidizes it rapidly.

$$HN_3 + HNO_2 \rightleftharpoons N_2O \uparrow + N_2 \uparrow + H_2O$$

In certain reactions it can behave as an oxidant.

$$HN_3 + H_2S \longrightarrow S \downarrow + NH_3 + N_2 \uparrow; \text{ oxidation of } S^{2-} \text{ and disproportionation}$$

$$Cu_2O \downarrow + 5HN_3 \rightarrow 2Cu(N_3)_2 \downarrow + NH_3 + N_2 \uparrow + H_2O; \text{ oxidation of } Cu^+ \text{ and disproportionation.}$$

Detection.—The red colour given by N_3^- with Fe^{3+} is used. The colour is due to the ion FeN_3^{2+}. CNS^- gives the same reaction. Iodides are oxidized to iodine. Ferri- and ferrocyanides should be separated by Cd^{2+}. F^-, $C_2O_4^{2-}$, etc., which complex Fe^{3+} must be counteracted by an excess of reagent. S^{2-}, $S_2O_3^{2-}$ interfere.

Concentration limit.—2.10^{-4} g.-ion/litre (10 p.p.m.).

NITROGEN

The solubility of nitrogen is 10^{-3}M.
It is practically unoxidizable and irreducible in solution.

N(I+) HYPONITRITES

Hyponitrous acid, $H_2N_2O_2$, is a weak acid. $pk_2 = 7.7$; $pk_1 = 11.7$. Rather unstable, it breaks down to $N_2O + H_2O$.

Nitrous oxide, N_2O, is soluble to the extent of 0·025M in water
Hyponitrites are known: $BaH_2(N_2O_2)_2$, $K_2N_2O_2$.
It is a reductant:

$$N_2O_2^{2-} + 4OH^- - 4e \rightleftharpoons 2NO_2^- + 2H_2O \quad E = -0.18 \text{ volt (calc.)}$$

Formal oxidation potential: ~ 0.3 volt at pH 14.

Permanganate, nitrous acid, and bromine, etc., oxidize it. Ferricyanide is in equilibrium with it, 0·60 volt at pH 0. Iodine oxidizes it in alkalis and not in acids. It is an oxidant, giving NH_2OH, NH_2NH_2, thus hyposulphites give N_2H_4. Stannous chloride reduces it only as far as NH_2OH.

N(III+) NITRITES

The very strong acid N^{3+} does not exist. HNO_2, yielding a blue solution, is not stable; it decomposes by disproportionation into NO and NO_3^-. NO oxidizes in the air yielding brown NO_2.

The nitrous anion NO_2^- is stable; $pk = 3.4$.

All nitrites are soluble. Only that of silver, pale yellow, is of fairly low solubility.

NO_2^- gives complexes, particularly with Co^{3+} : $Co(NO_2)_6^{3-}$; $K_2Na[Co(NO_2)_6]$ is of low solubility.

Equilibrium constants

$$HNO_2 \rightleftharpoons NO_2^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 3.4$$
$$Cu(NO_2)_3^- \rightleftharpoons Cu(NO_2)_2 + NO_2^-; \quad pk_3 = -1.0;$$
$$pk_2 = -1.0; pk_1 = 1.2$$
$$Ag(NO_2)_2^- \rightleftharpoons AgNO_2 \downarrow + NO_2^- \quad . \quad . \quad . \quad . \quad . \quad -0.8$$
$$AgNO_2 \downarrow \rightleftharpoons Ag^+ + NO_2^-. \quad . \quad . \quad . \quad . \quad . \quad . \quad 3.6$$
$$K_2Na[Co(NO_2)_6] \downarrow \rightleftharpoons 2K^+ + Na^+ + Co(NO_2)_6^{3-}. \quad . \quad . \quad . \quad 10.7$$
$$(NH_4)_2Na[Co(NO_2)_6] \downarrow \rightleftharpoons 2NH_4^+ + Na^+ + Co(NO_2)_6^{3-} \quad . \quad . \quad 11.8; 14.2$$

N(V⁺) NITRATES

Nitric acid, HNO_3, is a strong acid. All the nitrates are soluble, except certain basic ones of Hg(II), Bi(III) which are soluble in strong acids.

Unstable complexes with Ce(IV), Ag(II) are known.

$$BiONO_3\downarrow + 2H^+ \rightleftharpoons Bi^{3+} + NO_3^- + H_2O \quad . \quad 2\cdot6$$
$$ZrNO_3^{3+} \rightleftharpoons Zr^{4+} + NO_3^- \quad . \quad . \quad . \quad 0\cdot3$$
$$ThNO_3^{3+} \rightleftharpoons Th^{4+} + NO_3^- \quad . \quad . \quad . \quad 0\cdot7 \ (I = 0\cdot5)$$
$$PuNO_3^{3+} \rightleftharpoons Pu^{4+} + NO_3^- \quad . \quad . \quad . \quad 2\cdot9 \ (I = 2)$$

Redox

(1) $\quad NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O \quad E_0 = 0\cdot93 \text{ volt}$
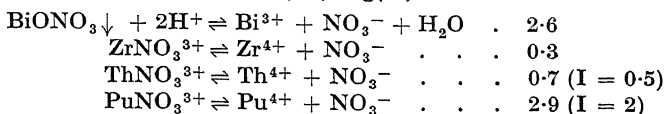
Formal E in volts . . .	0·93	1·00	1·10	
HNO_3	N	4N	12N	. . (I)

(2) $\qquad\qquad HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$
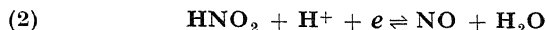
$$E = 0\cdot98 + 0\cdot06 \log \frac{|HNO_2|\cdot|H^+|}{pNO} \text{ volts} \quad . \quad . \quad (II)$$

pNO indicates the pressure of the nitric oxide in atmospheres.

In general, system (I) exchanges its electrons slowly in both directions; nitrates are only reduced at a reasonable speed in very acid solutions. However, with very powerful reductants the reduction can be effected in alkaline solutions.

The nitrites are oxidized slowly in acid solutions, more rapidly in more alkaline solutions.

The system (II) in general only reacts fast from the left to the right in acid solutions.

The reduction of NO_3^- at pH 0 is always followed by the reduction of nitrous acid, since the potentials of the two systems are very near to one another.

In system (I) the nitrites act as reductants. In system (II) they act as oxidants. Thus in acid solutions the nitrites reduce permanganate and oxidize iodides. In neutral or weak alkaline solution, I_2 oxidizes NO_2^-.

Nitric acid is reduced to NO, in particular by numerous metals such as Cu, Hg, etc., and Fe^{2+}.

Disproportionations.—In view of the closeness of the potentials of the two systems to one another at pH 0, HNO_2 is not stable and we have

$$3HNO_2 \rightleftharpoons NO_3^- + 2NO \uparrow + H_2O + H^+$$

(3) $\qquad\qquad NO_2^- + 8H^+ + 6e \longrightarrow NH_4^+ + 2H_2O$
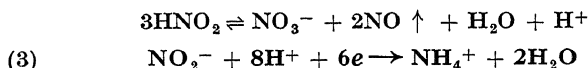
The reaction is very slow. In alkaline solutions $Fe(OH)_2$, Zn, Al and in acid solutions V^{2+}, Cr^{2+} reduce nitrates and nitrites to NH_3 or NH_4^+.

Detection of nitrites and nitrates

(1) **Redox indicators.**—Diphenylamine (0·75 volt) is oxidized to a blue compound.

Solution required.—0·5 g of diphenylamine in 100 ml of conc. sulphuric acid.

Procedure.—One drop of solution in $\frac{1}{2}$ ml of reagent.

Numerous oxidants give the same reaction (see p. 269).

Starch paste can be decolorized by nitrous fumes (0·9 volt).

(2) **Reduction by ferrous salts.**—Ferrous salts in acid, even acetic acid solution, reduce nitrites to NO. Nitrates are reduced in conc. sulphuric acid. The NO formed combines with ferrous ions to give the deep brownish-violet complex, $Fe(NO)_m^{2+}$.

Procedure.—Place $\frac{1}{2}$ ml of conc. sulphuric acid at the bottom of a small test-tube. Add a crystal of ferrous sulphate and heat until dissolved. Then cool under the tap and add, a little at a time, without mixing, the solution under examination. A brown ring of $Fe(NO)_m^{2+}$ is produced at the surface of separation of the two liquids.

Concentration limit.—10^{-3} g.-ion of NO_3^- per litre (60 p.p.m.).

Interfering substances.—Iodide ions give a brown ring of iodine at the surface of contact with the sulphuric acid. A large number of other ions can also interfere: Cl^- which gives $NOCl$; Br^-; CNS^- which is destroyed; similarly $Fe(CN)_6^{4-}$, CN^-, SO_3^{2-}, S^{2-}, $S_2O_3^{2-}$ interfere. Oxidants, CrO_4^{2-}, IO_3^-, ClO_3^-, $Mo(VI)$, $W(VI)$, etc., interfere.

A large number of these ions are eliminated by prior treatment with silver sulphate in neutral solution, followed by centrifuging. Chlorates should be reduced by sulphide dioxide before this separation.

Detection of nitrites.—(1) **Reducing power.**—In acid solution permanganate, in particular, is decolorized.

Interfering substances.—Numerous reducing ions give the same reaction. Oxidizing ions, which can co-exist with nitrites in neutral or alkaline solutions, can react when the solution is made acid.

(2) **Oxidizing power.**—Iodides are oxidized in acid solutions. Numerous oxidants give the same reaction.

(3) **Action of acids.**—Liberation of nitrous fumes. Very powerful oxidants and numerous reductants interfere.

(4) **Griess reagent.**—Nitrous acid reacts with a mixture of sulphanilic acid and α-naphthylamine giving a red azo dye.

$$H_2N\!-\!\hexagon\!-\!N\!=\!N\!-\!\hexagon\!-\!SO_3H$$
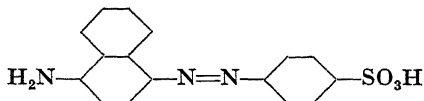
Solution required.—Dissolve 0·1 g of α-naphthylamine in 75 ml of water and 30 ml of pure acetic acid. Prepare also a solution of 0·5 g sulphanilic acid in 70 ml of water and 30 ml of acetic acid. Mix the two solutions.

Procedure.—To 2 drops of reagent add 1 drop of the solution initially diluted about twenty-fold.

Concentration limit.—10^{-5} g.-ion of NO_2^- per litre (0·5 p.p.m.).

Interfering substances.—The reaction is specific. However, powerful oxidants in acid solution interfere. Certain ions interfere in virtue of their own colour; Fe^{3+} can be complexed with tartrate ions. 0·01M $Cr(VI)$ gives a pink to violet coloration.

Notes.—The reaction can be used for detecting traces of nitrate after they have been reduced to nitrites.

Large quantities of reductants, e.g. S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, interfere in the reduction. They should be oxidized beforehand.

Procedure.—To 1 ml of solution, free from nitrite, add $9H$-H_2SO_4 until just acid and then 1 ml of 20 vol. hydrogen peroxide. Heat. Decant the solution and make the test with the Griess reagent in the presence of a little zinc powder.

Detection of nitrates in presence of nitrite.—The detection of nitrites is easy. The detection of nitrates in the presence of nitrites requires the destruction of the latter. Nitrites can be destroyed:

(1) *By HN_3.*—Nitrogen is liberated. To the neutral or weakly alkaline solution a 10 per cent NaN_3 in excess is added followed by acetic acid; in this way disproportionation in strong acid, which gives NO_3^-, is avoided. Boil. (HN_3 is toxic.)

(2) *By sulphamic acid NH_2SO_3H.*

NO_3^- can then be detected by one of the methods described.

Note.—Nitrites nearly always contain traces of nitrates.

IONS AND COMPOUNDS DERIVED FROM PHOSPHORUS

$$P = 32 \cdot 0$$

PHOSPHORUS is located in column V of the periodic classification below nitrogen and above arsenic. It resembles both these elements. In arsenic the cation As^{3+} still exists; but the corresponding cations of phosphorus and nitrogen do not, since they are too acid. The anions increase in stability in going from arsenic through phosphorus to nitrogen. Those corresponding to the oxidation state V^+ are very stable.

N
P
As
Sb

States of oxidation.—III^- in PH_3, II^- in P_2H_4, I^+ in H_3PO_2, III^+ in H_3PO_3, IV^+ in $H_4P_2O_6$ and V^+ in H_3PO_4.

PHOSPHORUS

It exists in several modifications, the most active of which is white phosphorus. In hot alkali, phosphorus disproportionates giving numerous compounds, among which are spontaneously inflammable phosphine, and the hypophosphites.

$$4P \downarrow + 3H_2O + 3OH^- \longrightarrow PH_3 \uparrow + 3H_2PO_2^-$$
$$2P \downarrow + H_2O + 2OH^- \longrightarrow PH_3 \uparrow + HPO_3^{2-}$$
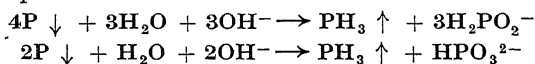
Oxidants attack phosphorus, which is a very strong reductant. For example, it is oxidized by iodine

$$P \downarrow + \tfrac{3}{2}I_2 \downarrow + 3OH^- \longrightarrow 3I^- + H_3PO_3$$
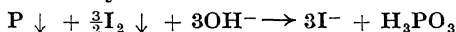
PHOSPHINE

PH_3, hydrogen phosphide or phosphine, is a gas. Its place in the periodic classification suggests its properties in relation to those of its neighbours. It is a weaker base than NH_3. Phosphonium iodide PH_4I is known in the solid state. It is destroyed in solution. In the phosphides P^{3-} behaves as a powerful base which reacts with water to give PH_3:

H₄Si | H₃N H₃P H₃As | H₂S

$$Ca_3P_2 \downarrow + 6H^+ \longrightarrow 2PH_3 \uparrow + 3Ca^{2+}$$
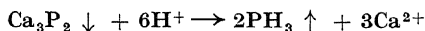
Black Ag_3P is of low solubility.

$$PH_4^+ \rightleftharpoons PH_3 \uparrow + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad 0$$

P(I) HYPOPHOSPHITES

Hypophosphorous acid H_3PO_2 is practically monobasic, $pk = 1$–2. The anions are colourless.

The hypophosphites are in general soluble: those of Pb(II) and of Th(IV) and U(IV) are of low solubility. They correspond to M_3PO_2.

Numerous complexes with cations are known. The salts on ignition give spontaneously inflammable PH_3.

Redox.—The hypophosphorous ion is a powerful reductant but acts slowly.

Ag^+, Hg^{2+}, As^{3+}, Cu^{2+} are reduced to metal in hot acid solution. In the presence of catalysts such as Pd(II) it becomes much more energetic. Methylene blue and hydrogen ions are then reduced.

P(III) PHOSPHITES

In the presence of water PCl_3 is destroyed with formation of phosphorous acid.

Phosphorous acid H_3PO_3 has in practice only two basicities of importance: $pk_3 = 1 \cdot 5 – 1 \cdot 8$; $pk_2 = 6 \cdot 2 – 6 \cdot 6$.

The alkali salts are soluble; the solubility of the others is low but they dissolve in strongly acid solution. Ag_2HPO_3 is white and gradually transforms to black silver. $BaHPO_3$ is white. On ignition the phosphites give spontaneously inflammable phosphine.

Redox.—Phosphites are reductants. They decolorize permanganate slowly. Ag^+, Hg^{2+} are reduced but As^{3+} and Cu^{2+} are not (difference from the hypophosphites); the action is slow. Iodine is reduced at pH 8·3.

P(V) PHOSPHATES

Phosphorus pentachloride PCl_5 and oxychloride $POCl_3$ are hydrolysed by water to phosphoric acid.

P_2O_5 is a white solid; it can give three acids: ortho-, pyro-, and metaphosphoric. The meta- and pyrophosphoric acids are in false equilibrium. They hydrolyse slowly, more rapidly in the hot and in acid solutions, giving the ortho-acid H_3PO_4 which is the stable hydroxide.

Orthophosphoric acid (H_3PO_4)

$pk_3 = 2 \cdot 2$; $pk_2 = 7 \cdot 2$; $pk_1 = 12 \cdot 3$. The last acidity is very weak. Only the alkali phosphates are soluble; the others are more or less soluble in acid solution.

Precipitation pH's of some phosphates (0·01M)

$MgNH_4PO_4$	. .	8·9	$AlPO_4$	. . . .	3·8
Ba, $CaHPO_4$	. .	5·5	$FePO_4$	. . . .	2·3
$Co_3(PO_4)_2$	. . .	5·3			(yellowish white)
$Ni_3(PO_4)_2$	. . .	6·3	$ZrOHPO_4$	. . .	1·6
Ag_3PO_4	. . .	5	$Pb_3(PO_4)_2$	. . .	low sol'ty at
(yellow; sol. in NH_3 and HNO_3)					pH 2
$Zn_3(PO_4)_2$	. . .	4·7	Hg_3PO_4	. . .	
			$BiPO_4$	. . . .	low sol'ty in
					dil. HNO_3

Complexes.—Numerous complexes are formed with ions of the aluminium group, and also with V(V), Mo(VI), W(VI); yellow ammonium phosphomolybdate is the best known.

Equilibrium constants

$$H_3PO_4 \rightleftharpoons H_2PO_4{}^- + H^+; \quad pk_3 = 2\cdot1\text{--}2\cdot2; \quad pk_2 = 7\cdot2;$$
$$pk_1 = 12\cdot3 \; (I = 0)$$

$Li_3PO_4 \downarrow \rightleftharpoons 3Li^+ + PO_4{}^{3-}$	$12\cdot5$
$Mg_3(PO_4)_2 \downarrow \rightleftharpoons 3Mg^{2+} + 2PO_4{}^{3-}$	$12\cdot6$
$AlPO_4\downarrow \rightleftharpoons Al^{3+} + PO_4{}^{3-}$	$6(?)$
$CePO_4\downarrow \rightleftharpoons Ce^{3+} + PO_4{}^{3-}$	$18\cdot5$
$MgNH_4PO_4 \downarrow \rightleftharpoons Mg^{2+} + NH_4{}^+ + PO_4{}^{3-}$ . . .	$12\cdot6$
$CaHPO_4 \downarrow \rightleftharpoons Ca^{2+} + HPO_4{}^-$	$5\cdot3\text{--}6\cdot6$
$Ca_3(PO_4)_2 \downarrow \rightleftharpoons 3Ca^{2+} + 2PO_4{}^{3-}$	25
$FeHPO_4 \rightleftharpoons Fe^{2+} + HPO_4{}^{2-}$	$9\cdot4$
$Ag_3PO_4 \downarrow \rightleftharpoons 3Ag^+ + PO_4{}^{3-}$	$20\cdot8$
$PbHPO_4 \downarrow \rightleftharpoons Pb^{2+} + HPO_4{}^{2-}$	$10\text{--}11\cdot4$
$Pb_3(PO_4)_2 \downarrow \rightleftharpoons 3Pb^{2+} + 2PO_4{}^{3-}$	$32\cdot0$
$BiPO_4 \downarrow \rightleftharpoons Bi^{3+} + PO_4{}^{3-}$	$20; 19$

Redox.—Phosphate ions cannot be reduced in solution, but only in the dry way.

Detection of phosphate ions.—The yellow ammonium phospho-molybdate, of low solubility in nitric acid, is precipitated. Reaction takes place in the cold but the presence of F^-, Cl^-, etc., delays the precipitation and in such cases an excess of reagent should be added and the solution heated.

Interfering substances.—As(V) gives in the hot a yellow precipitate of ammonium arsenimolybdate; silica gives a yellow coloration. These two reactions are inhibited by the addition of tartrate ions which complex As(V) and Mo(VI) sufficiently to inhibit the formation of the arseni- and silicomolybdate complexes, but not enough to prevent the formation of the phosphomolybdate complex which is less soluble. Chloride ions interfere. They are eliminated sufficiently by boiling the HCl solution with an excess of nitric acid for 1 minute.

Pyrophosphate ions momentarily inhibit the reaction. Reducing ions are oxidized by hot nitric acid.

$Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$ which give precipitates should be separated beforehand.

Solutions required

    (1) Molybdate reagent:

Ammonium molybdate	50 g
Ammonium nitrate	75 g
Water	700 ml
Then conc. HNO_3	300 ml

    (2) Tartaric acid: 15 g in 100 ml of molybdate reagent.

Procedure.—The majority of the chloride ion content is eliminated by boiling 1 drop of solution with 2 drops of conc. HNO_3. Add 2 drops of reagent. Transfer to a water bath. Wait. A yellow precipitate is formed in the presence of phosphoric acid.

Concentration limit.—10^{-3}M-H_3PO_4 per litre (at the end of 5 minutes) (100 p.p.m.).

Note.—Sn(IV) and Sb(III) precipitate on boiling with nitric acid. HCl can then be driven off by heating with sulphuric acid.

Polyphosphoric acids

Between pyrophosphoric acid $H_4P_2O_7$ and metaphosphoric acid $(HPO_3)_m$ (m = 3 or 6) a large number of condensed ions and molecules exist: $H_5P_3O_{11}$, $H_6P_4O_{13}$, etc.

Pyrophosphoric acid ($H_4P_2O_7$)

$$pk_4 = 0\cdot85; \quad pk_3 = 2\cdot0; \quad pk_2 = 6\cdot7; \quad pk_1 = 9\cdot6$$

On heating in nitric acid it hydrates, giving orthophosphoric acid. Only the alkali pyrophosphates are soluble. $Ag_4P_2O_7$, white, is of low solubility in acetic acid (difference from the phosphites and also from the phosphates). The barium salt is white. The magnesium salt $Mg_2P_2O_7$ is soluble in an excess of pyrophosphate ions because complexes are formed. $Zn_2P_2O_7$ is of low solubility at pH 3·7 (difference from the ortho and meta acids).

Numerous complexes are known, mainly with the elements of the aluminium and zinc groups.

With the molybdate reagent a yellow precipitate is obtained after converting to the ortho acid by prolonged heating.

Equilibrium constants

$$CeP_2O_7^- \rightleftharpoons Ce^{3+} + P_2O_7^{4-} \quad . \quad . \quad . \quad . \quad 7\cdot1$$
$$CuP_2O_7^{2-} \rightleftharpoons Cu^{2+} + P_2O_7^{4-} \quad . \quad . \quad . \quad . \quad 13\cdot2$$
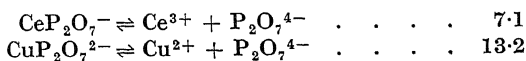
Metaphosphoric acids $(HPO_3)_m$

$(HPO_3)_4$: $pk_4 = 2\cdot6$; $pk_3 = 6\cdot4$; $pk_2 = 8\cdot8$ and $pk_1 = 11\cdot4$.
$(HPO_3)_6$: $pk_6 = 2$; $pk_5 = 5\cdot6$; $pk_4 = 7\cdot8$.
$(HPO_3)_3$ would be a strong acid.

The alkali and magnesium salts are soluble; the others are soluble in an excess of metaphosphate ions with formation of complexes. The white silver metaphosphate is soluble in ammonia. Zinc metaphosphate $Zn(PO_3)_2$ does not precipitate at pH 7 in presence of ammonium salts (difference from pyro- and orthophosphate).

By heating in dilute acids the pyro and meta acids are hydrolysed.

P(IV) HYPOPHOSPHORIC ACID $H_4P_2O_6$

$$pk_4 = 2\cdot2; \quad pk_3 = 2\cdot8; \quad pk_2 = 7\cdot3; \quad pk_1 = 10$$

Strong acids convert it in the hot to a mixture of phosphorous and phosphoric acids.

Many of the hypophosphates are of low solubility. The solubility of

some is low even in concentrated acids. The sodium salt is of low solubility and $Ag_4P_2O_6$ is of low solubility in nitric acid. $Ba_2P_2O_6$ is of low solubility in acetic acid. ThP_2O_6 and TiP_2O_6 are of low solubility in concentrated acid.

It is a reductant, weaker than phosphorous acid. It decolorizes permanganate and bromine.

CARBON COMPOUNDS

$$C = 12 \cdot 01$$

CARBON is to be found in the fourth column of the periodic table. In the IV^+ oxidation state it should be very acid and in the IV^- state it should be basic; the corresponding compounds CCl_4 and CH_4 have a very low solubility in water. Carbon can exist in other states of oxidation, in particular in II^+.

Redox.—In solution the important system is:

$$C(IV) + 2e \rightleftharpoons C(II)$$
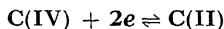
Electron exchange is in general slow in solution from right to left.

The reduction of $C(IV)$ to $C(II)$ is extremely slow. It can only be achieved, and then at an extremely slow rate, in the presence of catalysts and light. In practice the reduction of H_2CO_3, CO_2, CO_3^{2-} to CO, HCO_2H, HCO_2^- or $C_2O_4^{2-}$ cannot be achieved in solution.

$C(II^+)$ CARBON MONOXIDE, CO

A gas of low solubility (0·001M), colourless and odourless. Very toxic.

Redox

$$C(II) - 2e \rightarrow C(IV) \quad \text{or} \quad CO + H_2O - 2e \rightarrow CO_2 + 2H^+$$

CO is a reductant but acts extremely slowly. Certain substances plan the role of catalysts and reaction becomes possible: $I(V)$, Ag^+, finely divided Pt and Pd.

Detection.—(1) **Iodine pentoxide.**—A mixture of iodine pentoxide and fuming sulphuric acid is adsorbed on a finely divided inert support. Under these conditions CO is oxidized in the cold:

$$I_2O_5 \downarrow + 5CO \uparrow \rightarrow 5CO_2 \uparrow + I_2 \downarrow$$
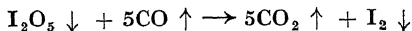
A green coloration is observed.

Interfering gases.—Other reductant gases can be adsorbed beforehand on active carbon which allows only CO to pass. Apparatus for achieving this has been described.

(2) **Palladous chloride** is reduced by carbon monoxide to palladium; a yellow coloration changing to brown and black. It is generally used in the form of test papers impregnated with the reagent.

Interfering gases.—Hydrocarbons, H_2 and H_2S.

(3) **Silver reagent.**—The complex $Ag(NH_3)_2^+$ gives a black precipitate of silver.

Interfering gases.—H_2, CH_4 do not interfere, but C_2H_4, C_2H_2 do so.

(4) **Mermeix reagent.**—The catalytic power of Ag^+ ions in the oxidation of CO can be used in the presence of MnO_4^- which is decolorized.

Solutions required

   (a) Potassium permanganate . . . 1 g
     Water . . . . 950 ml
     Nitric acid . . . . 50 ml
   (b) Silver nitrate . . . . 3 g
     Water . . . . 100 ml

Mix just before use 1 ml of (a) and 20 ml of (b). Then add 1 ml of HNO_3 and 50 ml of water.

One part of CO in 1000 parts of air can be detected.

Interfering gases.—Substances which reduce MnO_4^- interfere.

(5) **Blood method.**—Diluted blood mixed with a solution of tannin gives a grey suspension. If the blood has absorbed carbon monoxide the suspension remains bright red.

(6) **Toximeter.**—This is an apparatus consisting of an alcohol thermometer whose reservoir is covered with some spongy platinum. Oxidation of CO in the air in contact with the platinum causes a liberation of heat which is recorded by an expansion of the alcohol in the thermometer.

Interfering gases.—The other reductant gases, hydrogen, hydrocarbons, etc., give the same result. The apparatus is sensitive to changes of temperature.

C(II⁺) FORMATES

Formic acid, HCOOH, boils at 110°. It is miscible in water, and has a sharp odour. $pK = 3.7$.

Barium formate is soluble. Silver formate is of low solubility and in the hot is reduced to silver. The same thing happens with mercuric formate. On heating, formates carbonize slightly. In the main they yield carbon monoxide. Conc. sulphuric acid also gives CO by dehydration. With ferric salts there is a red coloration, destroyed in the hot. When treated with sulphuric acid and alcohol an ester with a fruity odour is produced.

Redox

$$HCO_2H - 2e \rightarrow CO_2 + 2H^+ \qquad E = -0.14 \text{ volt (calculated)}$$
$$HCO_2^- + 3OH^- - 2e \rightarrow CO_3^{2-} + 2H_2O \quad E = -0.95 \text{ ,, \qquad ,,}$$
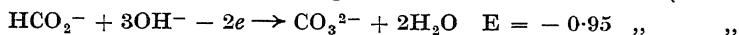
The system acts as a reductant very slowly, but becomes active in the presence of catalysts. Thus in the presence of finely divided Pd, $E = 0.02$ volt in $N\text{-}H_2SO_4$, -0.4 volt in $N\text{-}HCOONa$ and -0.7 volt in $N\text{-}KOH$. Formate ion reduces mercuric salts in the hot to mercurous salts and sometimes to mercury. The permanganate ion is reduced slowly.

ACETATES

Acetic acid, CH_3COOH, melts at $+17°$ and boils at $118°$. Miscible with water. Sharp odour. $pK = 4.8$.

Silver acetate is fairly soluble, 0.16 g.-mol/litre. The other acetates, except that of mercurous mercury, are soluble. Low-solubility basic acetates are known, e.g. that of Hg^{2+}.

Numerous complexes.—With Fe^{3+} a red complex which is destroyed in the hot with precipitation of the hydroxide.

Detection.—(1) **On heating**, acetates carbonize slightly and give off combustible products, acetone among them.

(2) **Ester.**—With alcohol in the presence of sulphuric acid ethyl acetate with a fruity odour is formed.

Procedure.—Take 1 ml of solution and make it alkaline with caustic soda. Evaporate to dryness. Redissolve with a $\frac{1}{2}$ ml of conc. H_2SO_4. Drive off HCN, SO_2, etc. Add 0·1 ml of alcohol and heat on a water bath.
Concentration limit.—1 mg of CH_3COOH per litre.

(3) **Cacodyl oxide.**—Solid acetates heated with arsenious oxide give cacodyl oxide having a characteristic odour.

Procedure.—Add 1 mg of As_2O_3 to several milligrams of solid and heat gently.

$$As_2O_3 + 4CH_3COOK \rightarrow (CH_3)_2AsOAs(CH_3)_2 + 2CO_2 + 2K_2CO_3$$
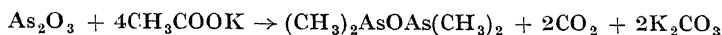
Interfering substances.—Tartrates should be precipitated with calcium or barium hydroxides and separated. S^{2-}, CNS^- should be precipitated by Hg(II). ClO_3^-, NO_3^-, NO_2^- should be reduced by a little zinc powder in HCl; boil and neutralize.
Concentration limit.—0·1 mg of acetate per litre.

The homologues of acetic acid: propionic, butyric, etc., have acidity constants which decrease as the molecules become heavier. The chlorinated derivatives are stronger acids: $ClCH_2CO_2H$; $pK = 2·7$; Cl_2CHCO_2H; $pK = 1·3$.

OXALATES

Oxalic acid, $H_2C_2O_4 . 2H_2O$, is crystalline and dibasic: $pk_2 = 1·2$; $pk_1 = 4·1$.

The oxalates are decomposed by heat into carbon monoxide and carbonates. Hot conc. sulphuric acid gives CO and CO_2.

The alkali oxalates are soluble; the others, excepting those of the rare earths, are soluble in acids.

Numerous complexes with Sn(IV), Mo(VI), V(IV), W(VI), Fe(III), Al(III), Cr(III), etc.

Equilibrium constants

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad 1·2$$
$$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+ \quad . \quad . \quad . \quad . \quad . \quad 4·1$$
$$Al(C_2O_4)_3^{3-} \rightleftharpoons Al(C_2O_4^-)_2^- + C_2O_4^{2-}; \quad pk_3 = 3·3;$$
$$pk_2 + pk_1 = 13·0$$
$$Ag_2C_2O_4 \downarrow \rightleftharpoons 2Ag^+ + C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad 11·0$$
$$BaC_2O_4 \downarrow \rightleftharpoons Ba^{2+} + C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad 6·8$$
$$Cd(C_2O_4)_2^{2-} \rightleftharpoons CdC_2O_4 + C_2O_4^{2-}; \quad pk_2 \sim 1·8; pk_1 = 3·5;$$
$$pk_1 + pk_2 = 5·7$$
$$CdC_2O_4 \downarrow \rightleftharpoons Cd^{2+} + C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad 7·8$$
$$CaC_2O_4 \downarrow \rightleftharpoons Ca^{2+} + C_2O_4^{2-} \quad . \quad . \quad . \quad . \quad . \quad 8·6$$
$$Ce(C_2O_4)_3^{3-} \rightleftharpoons Ce(C_2O_4)_2^- + C_2O_4^{2-}; \quad pk_3 = 0·8; pk_2 = 4·0; pk_1 = 6·5$$

21
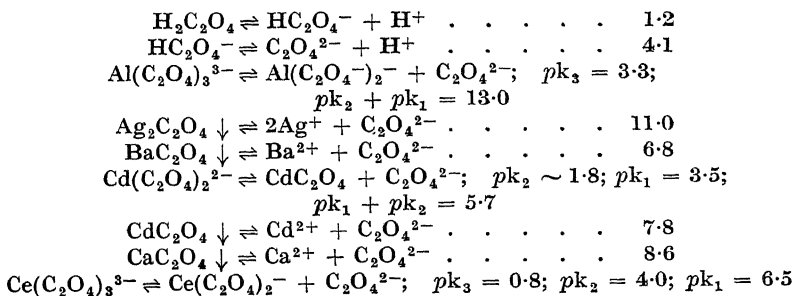
$$Ce_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Ce^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 28\cdot7$$
$$Co(C_2O_4)_2{}^{2-} \rightleftharpoons Co^{2+} + 2C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 6\cdot7$$
$$CuC_2O_4 \downarrow \rightleftharpoons Cu^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 7\cdot5$$
$$Fe(C_2O_4)_3{}^{4-} \rightleftharpoons Fe^{2+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 6\cdot2; \; 10\cdot0$$
$$FeC_2O_4 \downarrow \rightleftharpoons Fe^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 6\cdot7$$
$$Fe(C_2O_4)_3{}^{3-} \rightleftharpoons Fe(C_2O_4)_2{}^- + C_2O_4{}^{2-}; \quad pk_3 = 4\cdot0;$$
$$pk_2 = 6\cdot8; \; pk_1 = 9\cdot4 \; (I = 0)$$
$$In(C_2O_4)_2{}^- \rightleftharpoons In^{3+} + 2C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 8\cdot6$$
$$K[In(C_2O_4)_2] \downarrow \rightleftharpoons K^+ + In(C_2O_4)_2{}^- \quad . \quad . \quad . \quad . \quad 4\cdot4$$
$$La_2(C_2O_4)_3 \downarrow \rightleftharpoons 2La^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 27\cdot7$$
$$Mg(C_2O_4)_2{}^{2-} \rightleftharpoons Mg^{2+} + 2C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 4\cdot4$$
$$MgC_2O_4 \downarrow \rightleftharpoons Mg^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 4\cdot8$$
$$Mn(C_2O_4)_3{}^{4-} \rightleftharpoons Mn^{2+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 2\cdot4$$
$$MnC_2O_4 \downarrow \rightleftharpoons Mn^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 4\cdot4$$
$$Hg_2C_2O_4 \downarrow \rightleftharpoons Hg_2{}^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 13\cdot0$$
$$Nd(C_2O_4)_3{}^{3-} \rightleftharpoons Nd(C_2O_4)_2{}^- + C_2O_4{}^{2-}; \quad pk_3 \leqslant -1\cdot9;$$
$$pk_2 = 4\cdot6; \; pk_1 = 7\cdot3$$
$$Nd_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Nd^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 28\cdot2$$
$$Ni(C_2O_4)_2{}^{2-} \rightleftharpoons Ni^{2+} + 2C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 6\cdot5$$
$$NiC_2O_4 \downarrow \rightleftharpoons Ni^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 7\cdot0$$
$$PbC_2O_4 \downarrow \rightleftharpoons Pb^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 10\cdot5$$
$$Pr_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Pr^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 27\cdot3$$
$$Sm_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Sm^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 28\cdot5$$
$$Sc_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Sc^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 14\cdot5$$
$$SrC_2O_4 \downarrow \rightleftharpoons Sr^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 7\cdot2$$
$$UO_2(C_2O_4)_2{}^{2-} \rightleftharpoons UO_2C_2O_4 + C_2O_4{}^{2-}; \quad pk_2 = -1\cdot1; \; pk_1 = 5\cdot8$$
$$Yb_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Yb^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 24\cdot3$$
$$Yb(C_2O_4)_3{}^{3-} \rightleftharpoons Yb(C_2O_4)_2{}^- + C_2O_4{}^{2-}; \quad pk_3 \leqslant -1\cdot9;$$
$$pk_2 = 4\cdot6; \; pk_1 = 7\cdot3$$
$$Y_2(C_2O_4)_3 \downarrow \rightleftharpoons 2Y^{3+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 26\cdot3$$
$$Zn(C_2O_4)_3{}^{4-} \rightleftharpoons Zn^{2+} + 3C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad 9$$
$$ZnC_2O_4 \downarrow \rightleftharpoons Zn^{2+} + C_2O_4{}^{2-} \quad . \quad . \quad . \quad . \quad . \quad 8\cdot8$$

Redox

(1) $H_2C_2O_4 - 2e \rightarrow 2CO_2 + 2H^+$ $E_0 = -0\cdot49$ volt (calculated)

Slow reaction. It scarcely occurs except with oxidants whose potential is above $1\cdot25$ volts at pH 0 and in the hot. $MnO_4{}^-$ is reduced in hot acid. The calculated normal potential is much more reducing, $-0\cdot49$ volt, and in the presence of catalysts such as finely divided platinum, more energetic reductions are realized.

(2) Oxalic acid can be reduced by electrolysis.

Detection.—(1) Zirconium—alizarin.—This reagent is decolorized by oxalates as by F^- (see p. 257). If the reaction is negative it can be concluded that oxalates are absent.

(2) **Characterization.**—The following two properties can be utilized; collectively they are specific for oxalates: (*a*) calcium oxalate has a low solubility in acetic acid; (*b*) oxalic acid reduces permanganate in hot dilute sulphuric acid.

Procedure (Delaby and Gautier).—To 1 ml of the solution some drops of 2N-HCl and an excess of $CaCl_2$ are added. If precipitation of low-solubility chloride is feared, HNO_3 and $Ca(NO_3)_2$ may be used. If sulphate and chloride ions are present in appreciable quantity they come down, and are separated. Make the solution alkaline with ammonia. Numerous salts of calcium precipitate and in every case the oxalate. Separate the precipitate and take it up again with 9N acetic acid. Only calcium oxalate is left behind. To confirm this take a little of the precipitate washed with a little $4N-H_2SO_4$ and a drop of dilute permanganate, and heat. Decoloration occurs.

C(IV+) CARBONATES

Carbon dioxide is soluble in water to the extent of 0·04 g.-mol/litre. It can be driven out of solution by boiling or by passing a current of gas through it.

Carbonic acid H_2CO_3 is a weak and unstable acid; 99 per cent is in the state of CO_2 in solution. $pk_2 = 6\cdot4$; $pk_1 = 10\cdot2$. Since

$$\frac{|H^+| \cdot |HCO_3^-|}{|CO_2 \text{ total}|} = 10^{-6\cdot4}$$

it can be deduced that

$$\frac{|H^+| \cdot |HCO_3^-|}{|H_2CO_3|} = 10^{-3\cdot7}$$

Complexes.—Fairly unstable ones with Co(III), Be(II), Th(IV), U(VI), etc.

Equilibrium constants

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ . . .	3·7
$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$ . . .	6·4
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ . . .	10·2
$Li_2CO_3 \downarrow \rightleftharpoons 2Li^+ + CO_3^{2-}$ . . .	2·4
$Tl_2CO_3 \downarrow \rightleftharpoons 2Tl^+ + CO_3^{2-}$ . . .	3·9
$MgCO_3 \downarrow \rightleftharpoons Mg^{2+} + CO_3^{2-}$ . . .	5·0
$NiCO_3 \downarrow \rightleftharpoons Ni^{2+} + CO_3^{2-}$ . . .	6·9
$ZnCO_3 \downarrow \rightleftharpoons Zn^{2+} + CO_3^{2-}$ . . .	7·0
$CaCO_3 \downarrow \rightleftharpoons Ca^{2+} + CO_3^{2-}$ . . .	8·3
$CaHCO_3^+ \rightleftharpoons Ca^{2+} + HCO_3^-$ . . .	− 0·8
$BaCO_3 \downarrow \rightleftharpoons Ba^{2+} + CO_3^{2-}$ . . .	8·3
$SrCO_3 \downarrow \rightleftharpoons Sr^{2+} + CO_3^{2-}$ . . .	8·8–10
$Sr(HCO_3)_2 \rightleftharpoons Sr^{2+} + 2HCO_3^-$ . .	5·7
$CuCO_3 \downarrow \rightleftharpoons Cu^{2+} + CO_3^{2-}$ . . .	9·9
$Ag_2CO_3 \downarrow \rightleftharpoons 2Ag^+ + CO_3^{2-}$ . . .	11·1
$MnCO_3 \downarrow \rightleftharpoons Mn^{2+} + CO_3^{2-}$ . .	10·1
$FeCO_3 \downarrow \rightleftharpoons Fe^{2+} + CO_3^{2-}$ . . .	10·3
$PbCO_3 \downarrow \rightleftharpoons Pb^{2+} + CO_3^{2-}$ . . .	12·8
$CdCO_3 \downarrow \rightleftharpoons Cd^{2+} + CO_3^{2-}$ . . .	13·6
$Hg_2CO_3 \downarrow \rightleftharpoons Hg_2^{2+} + CO_3^{2-}$ . .	16
$CoCO_3 \downarrow \rightleftharpoons Co^{2+} + CO_3^{2-}$ . . .	12·0

Detection of carbonate.—Treat with a strong acid, boil, and trap the gases liberated in baryta. $BaCO_3$ precipitates. An excess of carbonic acid redissolves the precipitate. (Use the apparatus fig. 92 (p. 326).) Natural carbonates are difficult to attack. Heat with a non-volatile dilute acid, $HClO_4$ or H_2SO_4. Grind the solid finely.

Interfering substances.—Sulphites and thiosulphates should be oxidized beforehand with hydrogen peroxide. It is a good idea to test that the precipitate obtained does not contain any sulphites by acidifying and testing with a drop of permanganate.

CYANIDE DERIVATIVES

Cyanogen $(CN)_2$

The oxidation numbers involved are: $C(II^+)$ and $C(IV^+)$, $N(III^-)$. It is a colourless toxic gas. Solubility: 0·5 g.-mol of $(CN)_2$ per litre. In properties it resembles the halogens.

In alkali it disproportionates to cyanide and cyanate ($C(IV)$ or $CN(I^-)$ and $CN(I^+)$):

$$(CN)_2 + H_2O \rightleftharpoons CNO^- + CN^- + 2H^+$$

$C(II^+)$ CYANIDES

Hydrocyanic acid boils at 26°. It is miscible with water and soluble in alcohol and ether. It has a smell of bitter almonds. It is extremely toxic; 50 mg suffice to bring on death rapidly. Colourless. A weak acid $pK = 9·1$. Colourless anions. It is decomposed slowly by water in the cold and rapidly in the hot.

$$HCN + 2H_2O \rightarrow HCO_2^- + NH_4^+$$
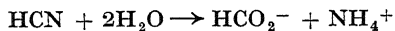
Below pH 9 HCN is liberated from cyanides and can be driven off and trapped in silver nitrate. AgCN precipitates. The cyanides of the alkalis and alkaline earths are soluble. Silver cyanide $Ag[Ag(CN)_2]$ is of low solubility in nitric acid. $Hg(CN)_2$ is soluble but very little ionized. The solubility of the majority of cyanides is low; but they are in general soluble in an excess of reagent giving complexes which are sometimes very stable. The complex cyanides with the elements of column Ib of the periodic table are particularly stable: $Cu(I)$, $Ag(I)$, and $Au(I)$. Those which are formed with the elements of column IIb decrease in stability in going from $Hg(II)$ to $Zn(II)$. Numerous complexes with $Fe(II)$, $Fe(III)$, $Co(III)$ and precious metals. $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ are practically un-ionized. They are less stable in acid solution because HCN is a very weak acid; in spite of this several of them are particularly stable and exist in quite strong acid. The complex cyanides when heated with mercuric acetate in solution are destroyed with formation of mercuric cyanide. Only $Co(CN)_6^{3-}$ resists this treatment. They are destroyed by conc. sulphuric acid in the hot yielding carbon monoxide and ammonium sulphate. Mercuric cyanide can be destroyed by H_2S with formation of mercuric sulphide.

Equilibrium constants

$$HCN \rightleftharpoons CN^- + H^+ \quad \ldots \quad \ldots \quad \ldots \quad 9\cdot1$$
$$Ag(CN)_4{}^{3-} \rightleftharpoons Ag(CN)_3{}^{2-} + CN^-; \quad pk_4 = 0; \ pk_3 = 1;$$
$$pk_2 + pk_1 = 20\cdot9$$
$$Ag[Ag(CN)_2] \downarrow \rightleftharpoons Ag^+ + Ag(CN)_2{}^- \quad \ldots \quad \ldots \quad 11\cdot4$$
$$Cd(CN)_4{}^{2-} \rightleftharpoons Cd(CN)_3{}^- + CN^-; \quad pk_4 = 3\cdot6; \ pk_3 = 4\cdot6;$$
$$pk_2 = 5\cdot1; \ pk_1 = 5\cdot5$$
$$Co(CN)_4{}^{2-} \rightleftharpoons Co^{2+} + 4CN^- \quad \ldots \quad \ldots \quad \ldots \quad 19\cdot1$$
$$Cu(CN)_4{}^{2-} \rightleftharpoons Cu^{2+} + 4CN^- \quad \ldots \quad \ldots \quad \ldots \quad 27\cdot3$$
$$Cu(CN)_3{}^{2-} \rightleftharpoons Cu(CN)_2{}^- + CN^-; \quad pk_3 = 11\cdot3(?); \ pk_2 = 4\cdot2;$$
$$CuCN \downarrow; \ pk_1 = 19\cdot5$$
$$Hg(CN)_4{}^{2-} \rightleftharpoons Hg^{2+} + 4CN^- \quad \ldots \quad \ldots \quad 40\cdot5; \ 41\cdot4; \ pk_4 \sim 3$$
$$Hg_2(CN)_2 \downarrow \rightleftharpoons Hg_2{}^{2+} + 2CN^- \quad \ldots \quad \ldots \quad 39; \ 39\cdot3$$
$$Ni(CN)_4{}^{2-} \rightleftharpoons Ni^{2+} + 4CN^- \quad \ldots \quad \ldots \quad \ldots \quad 15\cdot3; \ 22$$
$$Ni[Ni(CN)_4] \downarrow \rightleftharpoons Ni^{2+} + Ni(CN)_4{}^{2-} \quad \ldots \quad \ldots \quad 8\cdot8$$
$$Au(CN)_2{}^- \rightleftharpoons Au^+ + 2CN^- \quad \ldots \quad \ldots \quad \ldots \quad 21$$
$$Pb(CN)_4{}^{2-} \rightleftharpoons Pb^{2+} + 4CN^- \quad \ldots \quad \ldots \quad \ldots \quad 10\cdot3$$
$$Zn(CN)_4{}^{2-} \rightleftharpoons Zn(CN)_3{}^- + CN^-; \quad pk_4 = -1; \ +2\cdot7;$$
$$pk_3 + pk_2 + pk_1 = 17\cdot9$$

Redox

$$2CN^- - 2e \rightleftharpoons (CN)_2 \qquad E_0 = 0\cdot27 \text{ volt,}$$
$$2HCN - 2e \rightleftharpoons (CN)_2 + 2H^+ \quad 0\cdot80 \text{ volt at } pH \ 0$$

The oxidation is in general very slow in acid. $MnO_4{}^-$ only oxidizes CN^- very slowly; Ce^{4+} is inactive. In alkali of $pH > 13$ cyanogen disproportionates:

$$(CN)_2 \rightleftharpoons CN^- + CNO^-$$

and the overall system is then

$$CN^- + H_2O - 2e \rightleftharpoons CNO^- + 2H^+$$

In general CNO^- is only reduced very slowly.

In the presence of I^-, Br^-, Cl^- the cyanides are oxidized to CNI, CNBr, and CNCl. Similarly I_2 oxidizes CN^- to CNI (rapid).

We have $I_2 + 2CN^- - 2e \rightleftharpoons 2ICN \quad E_0 = 0.11$ volt

Detection

(1) **Silver salt.**—The silver salt has a low solubility in $4N$-HNO_3 and is soluble in an excess of HNO_3. AgCl, AgBr, AgN_3, AgCNS, $Ag_4Fe(CN)_6$, $Ag_3Fe(CN)_6$ behave the same. HCN can be separated by slight acidification of the solution with tartaric acid, $HCO_3{}^-$ or a current of CO_2. By warming, or bubbling a gas through, HCN is driven off and can be trapped in silver nitrate. The reaction then becomes specific.

(2) **Cupric sulphides.**—A black colloidal solution of cupric sulphide is dissolved by cyanide with formation of a cuprocyanide complex which is very stable.

Solutions required.—0·001N copper sulphate. 0·01M ammonium sulphide.
Procedure.—To a drop of copper sulphate add a drop of ammonium sulphide. The solution becomes black. Add 2 drops of the solution

being examined; the reagent is decolorized when cyanide ions are present.

Concentration limit.—$5 . 10^{-3}$ of CN^- per litre (100 p.p.m.). The reaction is specific.

C(IV$^+$) CYANATES

Cyanic acid, HCNO, is a weak acid; $pK = 3 \cdot 8$; stronger than HCN. The white, low-solubility AgCNO dissolves in dilute nitric acid (difference from the cyanide). Lead cyanate is of low solubility. The cyanate ions are gradually destroyed by water.

$$CNO^- + 2H_2O \rightleftharpoons CO_3^{2-} + NH_4^+$$
$$HCNO \rightleftharpoons CNO^- + H^+ \quad . \quad . \quad . \quad . \quad 3 \cdot 8$$
$$AgCNO \downarrow \rightleftharpoons CNO^- + Ag^+ . \quad . \quad . \quad . \quad 6 \cdot 6$$

Detection of cyanates.—A blue complex is formed with the salts of cobalt, analogous to the thiocyanate complex. Make the test in the presence of benzyl alcohol.

Interfering substances.—Cyanides interfere by formation of cobalti-cyanides which causes Co^{2+} to disappear; eliminate HCN at the start by passing CO_2 through. CNS^- gives the same reaction. Numerous reductants interfere.

THIOCYANATES

HCNS is a liquid of low stability. It is effectively a strong acid. The colourless ion CNS^- has properties similar to those of the halides, as has CN^- and CNO^-.

All thiocyanates are soluble except those of Ag(I), Hg(I), Hg(II), Cu(I), Pb(II), these become soluble in the hot. The barium salt is soluble in water. The silver salt, very little soluble, is of low solubility in nitric acid.

Numerous complexes which are frequently coloured: with Fe^{3+} red, with Co^{2+} blue, $Mo(CNS)_5$ red, etc.

The salts and the complexes are frequently soluble in ether, alcohol and acetone. They are destroyed by hot conc. H_2SO_4.

Equilibrium constants

$$HCNS \rightleftharpoons CNS^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad 0 \cdot 85$$
$$Ag(CNS)_4{}^{3-} \rightleftharpoons Ag(CNS)_3{}^{2-} + CNS^-; \quad p k_4 + p k_3 = 2 \cdot 4;$$
$$p k_2 + p k_1 = 8 \cdot 4; \, AgCNS \downarrow; \, p k_1 = 12 \cdot 0; \, 11 \cdot 2$$
$$Bi(CNS)_6{}^{2-} \rightleftharpoons Bi(CNS)_5{}^{2-} + CNS^-; \quad p k_6 + p k_5 = 0 \cdot 8;$$
$$p k_4 + p k_3 = 1 \cdot 2; \, p k_2 = 1 \cdot 1$$
$$Cr(CNS)_6{}^{3-} \rightleftharpoons Cr(CNS)_5{}^{2-} + CNS^-; \quad p k_6 = -1 \cdot 6; \, p k_5 = -0 \cdot 7;$$
$$p k_4 = 0 \cdot 3; \, p k_3 = 1 \cdot 0; \, p k_2 = 1 \cdot 7; \, p k_1 = 3 \cdot 1$$
$$CuCNS \downarrow \rightleftharpoons Cu^+ + CNS^- \quad . \quad . \quad . \quad . \quad . \quad 13 \cdot 4; \, 15 \cdot 0$$
$$Fe(CNS)_5{}^{2-} \rightleftharpoons Fe(CNS)_4{}^- + CNS^-; \quad p k_5 = 0 \cdot 02; \, p k_4 = 0 \cdot 8;$$
$$p k_3 = 1 \cdot 4; \, p k_2 = 1 \cdot 9; \, p k_1 = 2 \cdot 3; \, 2 \cdot 9$$
$$Hg(CNS)_4{}^{2-} \rightleftharpoons Hg(CNS)_3{}^- + CNS^-; \quad p k_4 = 0 \cdot 6; \, p k_3 = 1 \cdot 7;$$
$$p k_2 + p k_1 = 19 \cdot 7; \, p k_4 + p k_3 + p k_2 + p k_1 = 19 \cdot 3$$
$$Hg_2(CNS)_2 \downarrow \rightleftharpoons Hg_2{}^{2+} + 2CNS^- \quad . \quad . \quad . \quad . \quad 19 \cdot 5$$

$$Au(CNS)_6{}^{3-} \rightleftharpoons Au(CNS)_5{}^{2-} + CNS^-; \quad pk_6 = 0; \; pk_5 = 0;$$
$$pk_4 + pk_3 = 4\cdot3; \; pk_2 + pk_1 = 13$$

$$Au(CNS)_4{}^- \rightleftharpoons Au^{3+} + 4CNS^- \quad \ldots \ldots \quad 36; \, 37\cdot5$$
$$TlCNS \downarrow \; \rightleftharpoons Tl^+ + CNS^- \quad \ldots \ldots \quad 3\cdot8$$
$$VOCNS^+ \rightleftharpoons VO^{2+} + CNS^- \ldots \ldots \quad 0\cdot9 \; (I = 2\cdot6)$$
$$VCNS^{2+} \rightleftharpoons V^{3+} + CNS^- \quad \ldots \ldots \quad 1\cdot7\text{--}2\cdot0 \; (I = 2\cdot6)$$

Redox.—Thiocyanates are reductants in acid solution:

$$2CNS^- - 2e \rightleftharpoons (CNS)_2 \quad E_0 = 0\cdot77 \text{ volt (calculated)}$$

$(CNS)_2$ is practically non-existent in aqueous solution because it disproportionates:

$$3(CNS)_2 + 4H_2O \longrightarrow 5CNS^- + SO_4{}^{2-} + HCN + 7H^+$$

giving the overall system

$$CNS^- + 4H_2O - 6e \longrightarrow SO_4{}^{2-} + HCN + 7H^+$$

The formal oxidation potential is given by

$$E = 0\cdot57 - 0\cdot058 \log | \, CNS^- \, | \text{ volt (fig. 85A)}$$

Above pH 7·5 $(CNS)_2$ is practically non-existent even as an intermediate compound and:

$$E = 1\cdot17 + \frac{0\cdot058}{6} \log \frac{| \, H^+ \, |}{| \, CNS^- \, |} \text{ volts}$$

corresponding to

$$CNS^- + 4H_2O - 6e \longrightarrow SO_4{}^{2-} + CN^- + 8H^+ \quad \text{for } pH > 9\cdot1$$

FIG. 85A.—FORMAL REDUCTION POTENTIAL OF CNS^-
AS A FUNCTION OF pH

In alkaline solution the thiocyanates become much more reducing (fig. 85A). Reaction is slow from left to right, and does not take place in the other direction. Permanganate, conc. nitric acid, iodates, hydrogen peroxide are reduced in acid, and iodine in alkaline solution. Fe(III), Mo(VI), etc., are reduced to some extent.

In sufficiently alkaline solution the cyanide formed can be oxidized to cyanate, but this oxidation is still slower than that of CNS^-. We then have finally

$$CNS^- + 5H_2O - 8e \longrightarrow SO_4{}^{2-} + CNO^- + 10H^+$$

Detection of CNS⁻.—The red complex $FeCNS^{2+}$ is formed in strong acid solution (compare p. 165).

Solution required.—10 per cent ferric chloride.

Procedure.—To a drop of solution made acid with HCl add a drop of ferric salt.

Concentration limit.—5.10^{-4} g.-ion of CNS⁻ per litre (3 p.p.m.).

Interfering substances.—I⁻ is oxidized by Fe(III). $Fe(CN)_6^{4-}$ gives a precipitate of Prussian blue. They can be separated with lead nitrate. If ions which complex Fe(III) are present (oxalate, fluoride, etc.) an excess of reagent must be added.

Some compounds can reduce Fe(III) in acid solution; add an excess of reagent. If S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CN⁻, and NO_2^- are present drive them off beforehand in acid solution. Powerful oxidants such as BrO_3^-, NO_2^- can oxidize CNS⁻ in acid solutions slowly; the coloration disappears gradually.

N_3^- gives the same reaction.

Note.—HCNS can be extracted by ether and the reaction is then specific. For this, to a drop of solution, add 15 drops of sodium sulphite in saturated solution to reduce the oxidants, then a little ether, acidify with HCl to bring the concentration of the latter up to 0·5 N. Shake. Separate the ether. Add Fe(III).

Concentration limit.—2–3 p.p.m. CNS⁻.

FERROCYANIDES

Hydroferrocyanic acid gives the yellow anions $Fe(CN)_6^{4-}$ which are practically un-ionized.

The two first acidities of hydroferrocyanic acid are strong. The two others are fairly strong.

It is an extremely stable complex; it is however destroyed in conc. HCl in the hot, giving HCN, and by hot conc. H_2SO_4.

The alkali ferrocyanides are soluble; $CaK_2[Fe(CN)_6]$ and $MgK_2[Fe(CN)_6]$ are of low solubility; the barium salt only precipitates in concentrated solution. The solubility of the Ce(IV), Th(IV), Zr(IV) salts is low even in acids, difference from the corresponding ferricyanides.

The zinc salt is white, and of low solubility in strong acids. The white silver salt has a low solubility in ammonia and nitric acid but is soluble in CN⁻. Numerous ferrocyanides are coloured; with ferric ions, Prussian blue is obtained. The uranyl and cupric salts are brown.

The low-solubility ferrocyanides are rendered soluble by boiling them in strong alkali.

Equilibrium constants

$$H_2[Fe(CN)_6]^{2-} \rightleftharpoons H[Fe(CN)_6]^{3-} + H^+ \quad . \quad . \quad . \quad 3$$
$$H[Fe(CN)_6]^{3-} \rightleftharpoons [Fe(CN)_6]^{4-} + H^+ \quad . \quad . \quad . \quad 3\cdot3\text{–}4\cdot3$$
$$Ag_2[Fe(CN)_5NO] \downarrow \rightleftharpoons [Fe(CN)_5NO]^{2-} + 2Ag^+ \quad . \quad . \quad 12\cdot1$$
$$Ag_4[Fe(CN)_6] \downarrow \rightleftharpoons [Fe(CN)_6]^{4-} + 4Ag^+ \quad . \quad . \quad . \quad 40\cdot8$$
$$K_2Zn_3[Fe(CN)_6]_2 \downarrow \rightleftharpoons 2K^+ + 3Zn^{2+} + 2Fe(CN)_6^{4-} \quad 95$$
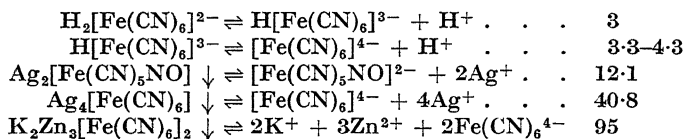
Detection

Formation of Prussian blue in acid solution with Fe(III)

Solution required.—10 per cent ferric chloride.

Procedure.—To a drop of the acidified test solution add a drop of reagent.

In the presence of ferrocyanide there is an intense blue coloration.

Concentration limit.—10^{-4} g.-ion of $Fe(CN)_6{}^{4-}$ per litre (20 p.p.m.).

Interfering substances.—Much I^- interferes, due to formation of iodine. Add an excess of reagent and drive off the iodine by heating.

If reductants are present an excess of reagent must be added and under these conditions $Fe(CN)_6{}^{3-}$ gives a similar reaction with the Fe(II) formed. Oxidants can oxidize $Fe(CN)_6{}^{4-}$ in acid solution. Much CNS^- interferes on account of the red coloration it produces.

Ions which form complexes with Fe(III), such as $C_2O_4{}^{2-}$, F^-, must be counteracted by adding an excess of reagent (10 per cent Fe(III) solution).

$NO_2{}^-$, S^{2-}, $S_2O_3{}^{2-}$, $SO_3{}^{2-}$ are eliminated by heating in acid solution.

FERRICYANIDES

The ferricyanide anions, $Fe(CN)_6{}^{3-}$, are orange, and practically un-ionized. They decompose slowly in the light. The acid is strong in all three dissociations. The orange silver salt, of low solubility in nitric acid, is soluble in ammonia (difference from the ferrocyanide). The soluble salts are those of the alkalis, alkaline earths, rare earths, Th(IV) and Fe(III). The others are of low solubility, even in acids (including the Cd(II) salt). Fe(III) gives a brown coloration.

With Fe(II) Turnbull's blue is formed (see p. 167).
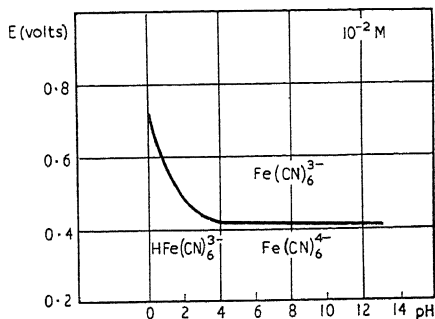
FIG. 86.—FORMAL NORMAL POTENTIAL OF THE REDOX SYSTEM
$Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ AS A FUNCTION OF pH

Redox

$$Fe(CN)_6{}^{3-} + e \rightleftharpoons Fe(CN)_6{}^{4-} \quad E_0 = 0.36 \text{ volt}$$

Formal potentials

0·41 volt at pH 4–13 (for 0·01M) (fig. 86).

0·7 volt in N-HCl, 0·56 volt in 0·1N-HCl.

0·72 volt in N-HClO$_4$ or N-H$_2$SO$_4$.

0·46 volt in 0·01N-NaOH; and 0·52 in 5N-NaOH.

Below pH 4, ferrocyanic acid is re-formed, and the apparent potential increases. According to the potential values quoted, the ferricyanides should often act as oxidants and the ferrocyanides frequently as reductants.

At pH 0 ferrocyanides are oxidized by permanganate.

Ferricyanides can often act as oxidants, being more energetic in proportion as the ferrocyanide ions produced are removed from the sphere of action (as insoluble salts). This can be done by adding a zinc salt, since zinc ferrocyanide is of low solubility in acid solution. Under these conditions, the ferricyanides oxidize the iodides quantitatively to iodine (p. 99). They oxidize S^{2-}, SO_3^{2-}, $Fe(OH)_2$. In alkali, the ferricyanide ion oxidizes a large number of systems.

Detection of ferricyanides.—With Fe(II) in acid solution ferricyanides give a precipitate of Turnbull's blue.

Solution required.—Solution of ferrous sulphate (5 per cent) in M-H_2SO_4.

Procedure.—To a drop of solution, acidified, add a drop of reagent. A blue precipitate or coloration appears.

Concentration limit.—10^{-4} g.-ion of $Fe(CN)_6^{3-}$ per litre (20 p.p.m.).

Interfering substances.—$Fe(CN)_6^{4-}$ gives a similar reaction with small quantities of Fe(III) contained in the reagent. Compounds which reduce $Fe(CN)_6^{3-}$ in acid solution: I^-, $S_2O_3^{2-}$, NO_2^-, or which oxidize the reagent: BrO_3^-, IO_3^-, etc., interfere. All these ions can be separated by prior precipitation with lead acetate.

COBALTICYANIDES $Co(CN)_6^{3-}$

The anion is a practically un-ionized complex; the acid $H_3Co(CN)_6$ is strong in all its dissociations. The soluble cobalticyanides are those of the alkalis, alkaline earths, Hg(II), Fe(III); those of low solubility are those of Ag(I), Co(II) pink, Ni(II) blue, Cd(II), Zn(II), Cu(II), all soluble in NH_3, little soluble in HNO_3; Fe(II) white, Hg(I) white, low solubility in HNO_3.

The cobalticyanides are destroyed by heating with conc. H_2SO_4.

Redox

$$Co(CN)_6^{4-} - e \rightleftharpoons Co(CN)_6^{3-} \quad E_0 = -0.83 \text{ volt}$$

IONS AND COMPOUNDS DERIVED FROM SILICON

SILICON

Si = 28·06

IN the periodic classification, silicon appears in column IV, between carbon and germanium. It has two main oxidation states: IV^+ and IV^-.

Si.—It is not attacked by acids, but is attacked by hot caustic soda, with liberation of silicon hydride (silane, silico-methane). This is a disproportionation.

$$2Si \downarrow + 2OH^- + H_2O \rightleftharpoons SiO_3^{2-} + SiH_4 \uparrow$$
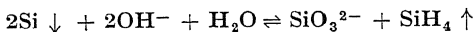
Si(IV).—Silane, SiH_4. Numerous silicides. The latter are decomposed by caustic soda, with liberation of spontaneously inflammable SiH_4; they are also decomposed by nitric acid, with formation of silica, SiO_2.

Si(IV+) SILICATES

The Si^{4+} cation does not exist, even in very acid solution; $SiCl_4$ reacts with water producing silicic acid. The hydroxide $Si(OH)_4$ or H_2SiO_3 precipitates even in very acid solution, and dissolves in solution of pH 12–13.

Hydrated silica can remain in colloidal solution right up to pH 0. NH_4^+, gelatine, etc., flocculate it. It can be made practically insoluble and filterable by evaporating to dryness in strong acid solution. The precipitate rapidly develops.

The silicates of Na^+ and K^+ are soluble. The solutions contain colloidal silica and condensed ions as well. With silver salts, a precipitate of silica mixed with silver oxide, Ag_2O, is formed; it is soluble in nitric acid and in ammonia. Barium silicate is soluble in acids.

Reaction with HF.—SiO_2 reacts with HF in the presence of dehydrating agents such as conc. H_2SO_4, yielding gaseous SiF_4:

$$SiO_2 \downarrow + 4HF \longrightarrow SiF_4 \uparrow + 2H_2O$$
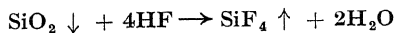
Silicon fluoride reacts with water giving the complex fluosilicate ion and silica:

$$3SiF_4 \downarrow + 4H_2O \longrightarrow 2SiF_6^{2-} + Si(OH)_4 \downarrow + 4H^+$$

In aqueous solution and in the presence of an excess of HF, only H_2SiF_6 is produced, which can be distilled as an azeotrope with water.

Insolubilization of silica.—It is difficult to precipitate silica completely. Usually, it is taken to dryness on a water bath with an excess of HCl, then dried for a further half an hour in an oven at 110°. It is then treated with dilute acid and the mixture filtered. The majority of the silica remains on the filter.

The process of rendering silica insoluble can be effected more easily

with H_2SO_4 or $HClO_4$. The mixture can in these cases be heated to the much higher boiling point of the acids (i.e. until 'white fumes' are seen).

Gelatine flocculates silica in the hot in an easily filtered form.

Complexes.—With Mo(VI) yellow silicomolybdic complexes of low stability are formed. The fluosilicate complex $SiF_6{}^{2-}$ and small amounts of $SiF_5{}^-$ and SiF_4 are fairly unstable. Many of the complexes are of low solubility; thus sodium aluminosilicate does not dissolve appreciably in alkali.

Equilibrium constants

$$H_2SiO_3 \downarrow \rightleftharpoons HSiO_3{}^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad 9\cdot5$$
$$HSiO_3{}^- \downarrow \rightleftharpoons SiO_3{}^{2-} + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad 11\cdot8$$
$$SiF_6{}^{2-} + 2H_2O \rightleftharpoons SiO_2, aq. \downarrow + 4H^+ + 6F^- \quad . \quad . \quad . \quad 26\cdot7$$
$$SiF_6{}^{2-} \rightleftharpoons SiF_4 \uparrow + 2F^- \quad . \quad . \quad . \quad . \quad . \quad . \quad 7\cdot2$$
$$SiF_4 \uparrow + 2H_2O \rightleftharpoons SiO_2 \downarrow + 4HF \quad . \quad . \quad . \quad . \quad . \quad 8$$
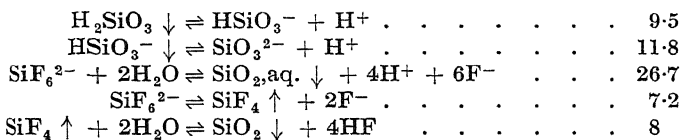
Detection of silica

(1) **By insolubilization** (see above).—The silica is separated, at first in the gelatinous condition, then in the form of powder. F^- interferes, since it converts the Si to H_2SIF_6.

(2) **By precipitation with gelatine.**—If a solid has to be examined, get it into solution first by fusing it with a little of a mixture of 3·4 g of fusion mixture ($Na_2CO_3 + K_2CO_3$) and 2·3 g of borax, in a platinum crucible (see dry decomposition, p. 340). Take up with 6N-HCl. Filter. Add conc. HCl and 0·5–1 ml of gelatine solution freshly prepared (1·5–5 per cent). Warm to 60°. The silica precipitates.

Interfering substances.—Zr(IV), Th(IV), Ti(IV) in the presence of H_3PO_4, Nb(V), Ta(V), Mo(VI), are also precipitated by gelatine which flocculates their hydroxides. They should be separated beforehand by prolonged boiling of the alkaline solution obtained by dissolving the fusion. Only Mo(VI) then remains in solution.

(3) **Formation of silicon fluoride.**—In a platinum or lead crucible, mix well together a little of the powdered solid to be examined with potassium fluoride. Wet the mix with conc. H_2SO_4. Suspend a drop of water on the underside of the crucible lid. The SiF_4 formed reacts with water, and the drop of water is seen to be covered with a film of gelatinous silica. Wait a few hours or heat for half an hour.

It is difficult to demonstrate the presence of silica in some natural silicates in this manner. The detection must be made by making a preliminary alkaline fusion: the alkali silicate thus formed is dissolved. The silica can be precipitated by boiling with an excess of ammonium chloride.

FLUOSILICATE ION

Fluosilicic acid is a strong acid, and, in concentrated solution, is a liquid which fumes in the air. With water it yields an azeotrope.

The solubility of the potassium and barium salts is low, and is also low in acid solution. Silver salts do not give a precipitate. The majority of the salts are soluble.

Concentrated sulphuric acid liberates silicon fluoride and hydrogen fluoride from the fluosilicates.

$SiF_6{}^{2-}$ is decomposed above pH 4:

$$SiF_6{}^{2-} + 4OH^- \longrightarrow Si(OH)_4 \downarrow + 6F^-$$
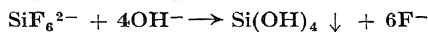
for example by $NH_3 + NH_4{}^+$; this occurs rapidly in the hot.

F^- can be detected by the alizarin-zirconium reagent (p. 257) since the fluosilicate complex is of fairly low stability. The silicon can be detected with the molybdate reagent after addition of an excess of boric acid, which masks F^-.

IONS AND COMPOUNDS DERIVED FROM BORON

BORON

$$B = 10\cdot82$$

BORON has only one important state of oxidation: III^+, but compounds in which it is in the III^- state are known. In the periodic table it is found in group III, above aluminium and between beryllium and carbon. The B^{3+} ion is nearly as acid as the Si^{4+} ion, a point of similarity between the two elements.

II	III	IV
Be	B	C
	Al	Si

Boron fluoride, which is obtained under the same conditions as silicon fluoride, is completely decomposed by water; a part of the B(III) passes into the state of complexes such as BF_4^-:

$$4BF_3 \uparrow\ + 3H_2O \longrightarrow 3BF_4^- + 3H^+ + B(OH)_3$$

Boric acid H_3BO_3, a white solid, is fairly soluble in cold water— 0·9M. It is less soluble in HCl, 0·3M in 10N-HCl. Its solubility is larger in the hot: 6M at 100°. It is slightly volatile in water vapour. Boric acid is very weak even in its strongest dissociation, $pK = 9\cdot2$. BO_2^- and condensed ions such as $B_4O_7^{2-}$, $B_2O_5^-$, etc., exist.

Low-solubility compounds.—All the borates are of low solubility in water, except those of the alkalis; they are all soluble in weak acid.

Barium borate, of low solubility, is soluble in acids and even in ammonium salts. Silver borate $AgBO_2$ is obtained mixed with silver oxide Ag_2O, and is soluble in NH_4^+.

Complexes.—BF_4^-, BF_3OH^-, etc., are fairly stable. There are numerous complexes with Mo(VI), W(VI), V(V), P(V), As(V). In combination with the polyalcohols such as glycerol, boric acid yields stronger acids. With an excess of mannitol, more stable complexes are obtained— $pK_A = 4$. With glycerol, $pK_A = 7\cdot5$. Complexes are formed with all hydroxylated organic compounds.

Equilibrium constants

$$H_3BO_3 \rightleftharpoons H_2BO_3^- + H^+; \quad pk_3 = 9\cdot2;\ pk_2 = 12\cdot7;$$
$$pk_1 = 13\cdot8$$
$$H_2B_4O_7 \rightleftharpoons HB_4O_7^- + H^+; \quad pk_2 \sim 4;\ pk_1 \sim 9$$

$4H_3BO_3 \rightleftharpoons HB_4O_7^- + H^+ + 5H_2O$	7·0
$H_3BO_3 + glyc. \rightleftharpoons H_3BO_3glyc.$	0
$HBO_2glyc. \quad \rightleftharpoons BO_2glyc.^- + H^+$	6·5
$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$	2·6
$HBF_3OH + H_2O \rightleftharpoons HBF_2(OH)_2 + HF$	2·0
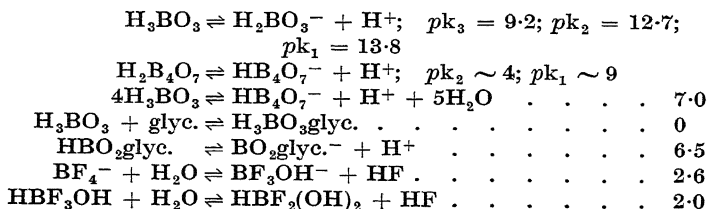
Detection of borates

(1) **Flame coloration.**—(*a*) Boric acid or the borates in admixture with H_2SO_4 colours the flame green. BF_3 (or borates $+$ CaF_2 $+$ H_2SO_4) at 200° (cold part of the laboratory gas flame) gives a still more sensitive green coloration.

Limit of sensitivity.—About 10^{-3} mg of boron.

(*b*) Minerals are decomposed with pyrosulphate. Sometimes a little fluoride is added and the mixture is heated in a platinum wire loop. A green flame is obtained.

(*c*) Boric ester.—With methyl alcohol, the borates in the presence of conc. sulphuric acid yield methyl borate which burns with a green flame.

Procedure.—To a little borate in a small test-tube, add about $\frac{1}{2}$ ml of conc. H_2SO_4 and 1 ml of methyl alcohol. Set fire to the alcohol—the flame is coloured green.

Interfering substances.—Salts which colour the flame green, copper, thallium, and barium interfere. They should be separated beforehand with Na_2CO_3, or use the apparatus shown in fig. 87 through which a current of air is blown. Ignite the gas at the mouth of the lead-off tube. The reaction is then specific. F^- does not interfere.

Limit of sensitivity.—0·2 mg of borate.

Note.—This reaction frequently does not take place with minerals which are difficult to attack. These should be subjected to alkaline fusion so as to get the borates into solution.

(2) **Turmeric paper.**—An acid borate solution gives a red stain on turmeric paper which becomes pink on drying. Then add 0·2N-NaOH; the stain becomes blue to green.

Concentration limit.—10^{-4} g.-mol of H_3BO_3 per litre (or 6 p.p.m.).

FIG. 87

Interfering substances.—Oxidants such as H_2O_2, NO_2^-, CrO_4^{2-}, ClO^-, IO^- as well as I^- interfere. F^- weakens the intensity of the stain.

(3) **Quinalizarin.**—This substance in solution in conc. H_2SO_4 changes colour from red to blue in the presence of borates.

Solution required.—0·1 per cent solution of quinalizarin in conc. H_2SO_4.

Procedure.—To $\frac{1}{2}$ ml of reagent, add a drop of the solution under examination.

Interfering substances.—A certain number of cations, such as Fe^{3+}, interfere, because their sulphates are precipitated in conc. H_2SO_4. They can be separated by boiling with 4N-NaOH and then filtering.

Fluorides, which give BF_4^-, inhibit the reaction.

Oxidants such as NO_3^-, ClO_3^-, $Fe(CN)_6^{3-}$ interfere, and should be reduced with hydrazine. Ge(IV) gives the same reaction.

Concentration limit.—$2 . 10^{-5}$ g.-mol of H_3BO_3 per litre (1 p.p.m.).
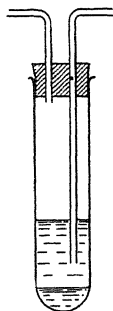
FLUOBORATE ION

HBF_4 is a fairly strong acid, giving an azeotropic mixture with water. It gives the reaction for F^- with zirconium-alizarin reagent and that for B by the formation of methyl borate.

KBF_4 is of fairly low solubility.

$$BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF \quad . \quad . \quad . \quad . \quad 2\cdot6$$
$$HBF_3OH + H_2O \rightleftharpoons HBF_2(OH)_2 + HF \quad . \quad . \quad . \quad 2\cdot0$$
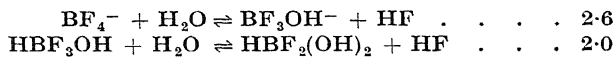
PART III

TECHNIQUE AND METHOD OF QUALITATIVE ANALYSIS

CHAPTER I

TECHNIQUE

THE methods used are as follows:

(1) MICROCHEMICAL TECHNIQUE.—The operations are carried out under the microscope by a special technique which uses, in the main, capillary tubes. This special technique is useful when only very small quantities of material are available. In this way all the usual operations can be carried out on quantities of matter of the order of a few milligrammes to a few γ (10^{-6} g) in a few λ (mm³).

A description of these methods will be found in the works mentioned in the bibliography to this chapter, in particular that of Benedetti-Pichler.

A more general technique is the identification of ions by the formation of characteristic crystals which are examined under the microscope. We have seen several examples of this in Part II. For more details consult the book by Chamot and Mason.

(2) SEMI-MICROTECHNIQUE, SPOT TESTS OR DROP REACTIONS.—This is the method most widely used nowadays and it is the one which we have adopted.

The reactions are carried out on a very reduced scale, using drops of the solution being examined and of the reagents, either on spot plates, or in (preferably conical) micro-centrifuge tubes, sometimes in small test-tubes, sometimes on paper.

Spot plates.—These are of porcelain and contain cavities large enough for several drops of the solutions to be mixed in them. They are useful for the observation of colorations or the formation of coloured precipitates. Black spot plates are useful for observing white precipitates.

Pipettes.—A series of pipettes whose tips are drawn down to give drops of 0·03 ml are used. The pipettes are closed by a rubber teat at their upper ends.

For reactions observed with a microscope, pipettes capable of giving drops of 0·01 ml must be available.

The pipettes are rinsed successively in water in two beakers. They are dried before use in an oven, if necessary.

Conical micro-centrifuge tubes (see fig. 88).—The majority of reactions are effected in conical micro-centrifuge tubes. They are shaped to suit the centrifuge available. The conical bottom of the tubes permits the observation of small quantities of precipitates, or of colorations in a few drops.

They are dried in an oven if necessary.

Test-tubes.—Tubes holding 5 ml and having the same diameter as the centrifuge tubes are useful.

Stirring rods.—Stirring rods with drawn-down ends are used. They are useful for stirring, especially in the depressions of spot plates.

They are rinsed in succession in the water in the two beakers already referred to.

Reagents.—The dissolved reagents are stored in small polythene bottles holding 15–30 ml provided with drawn-out tubes which give drops of 0·03 ml.

Solids are dispensed with a spatula (fig. 89).

Water bath (fig. 90).—It can be made up from a beaker covered with a circular piece of aluminium having four holes in it.

Tubes inserted through the openings in the cover of the water bath are fitted with annular rubber rings to prevent them falling through into the water.

FIG. 88.—CONICAL MICRO-CENTRIFUGE TUBE. $\frac{1}{2}$ SCALE

FIG. 89.—SPATULA. $\frac{1}{4}$ SCALE
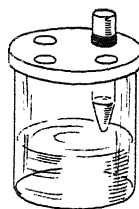
FIG. 90.—WATER BATH. $\frac{1}{4}$ SCALE

Separation and washing of precipitates.—Precipitation is carried out in a centrifuge tube. The precipitate is then centrifuged out by means of a hand centrifuge or, better, by an electrically driven high-speed centrifuge. The supernatant liquid is withdrawn by means of a pipette (fig. 91), or if the liquid is to be discarded, it is simply decanted.

Then add the wash liquid, stir or shake, and centrifuge once again.
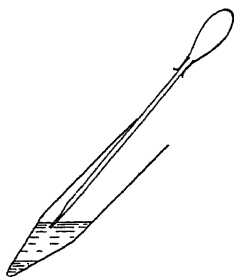
FIG. 91.—SEPARATION OF A PRECIPITATE. $\frac{1}{2}$ SCALE

(a) *(b)*
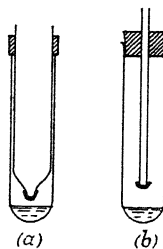
FIG. 92.—REACTIONS INVOLVING GASES. $\frac{1}{2}$ SCALE

Reactions on paper.—Reactions are carried out by depositing drops of the solution under examination on strong filter paper which has been impregnated with the reagent. The adsorbent properties of the paper and the rates of diffusion of the ions permit separations to be made on the surface of the paper.

Again, the reagents can be mixed directly on the paper. In addition to the advantages of separations which are achieved in this manner, the

properties of precipitates can be modified by the fine state of division in which they are formed and by the fact that they are adsorbed on paper.

They can be dried and heated over a flame, caused to react with gases, etc.

Reactions with gases.—If it is desired to detect a gas which is liberated from a solution, one of the two forms of apparatus as shown in fig. 92 is used. The internal tube in the form (*a*) is held in place with a rubber ring. A drop of the reagent is placed on the lower part of the internal tube (*a*) or on the stirring rod (*b*).

Other apparatus.—It is necessary to have a small porcelain or, better, silica crucible of 5-ml content.

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CHAMOT, E. M., and MASON, C. W., *Handbook of chemical microscopy*, 2 vols., John Wiley, New York, 1940.

BELCHER, R., and WILSON, C. L., *Qualitative inorganic microanalysis*, Longmans, Green, New York, 1946.

Semi-microchemical technique

See the bibliography, page 342.

CLASSICAL AND NEW METHODS OF CONDUCTING A QUALITATIVE ANALYSIS

DETECTION OF CATIONS. CLASSICAL METHOD

IN the classical method, the different elements are separated into groups, and then, within each group, each element is isolated by successive separations prior to its characterization. The different groups used in the classical method are the following:

(1) **Ions whose chlorides are of low solubility in acid.**—Ag(I), Hg(I), Pb(II), Tl(I).

(2) **Hydrogen sulphide group.**—Sulphides of low solubility in dilute HCl.

    (*a*) Sulphides soluble in S^{2-}:

        As(III), As(V), Sb(III), Sb(V), Sn(IV) and Ge(IV);

        Mo(VI), W(VI), V(V);

        Se(IV), Te(IV);

        Gold, platinum, and the metals of the platinum group.

    (*b*) Sulphides whose solubility in alkali is low:

        Hg(II), Cu(II), Pb(II), Cd(II), Bi(III).

(3) **Ammonium sulphide group**

    (*a*) Hydroxides whose solubility in $NH_3 + NH_4^+$ is low:

        Be(II);

        Al(III), Fe(III), Cr(III), Tl(III), rare earths (III);

        In(III), Ga(III);

        Ce(IV), Ti(IV), Zr(IV), Th(IV), V(IV);

        Nb(V), Ta(V).

    (*b*) Sulphides soluble in acid, but of low solubility in ammonia:

        Fe(II), Mn(II), Zn(II), Ni(II), Co(II).

(4) **Alkaline earths**

    Ca(II), Sr(II), Ba(II);

    Mg(II).

(5) **Alkalis**

    Li(I), Na(I), K(I), NH_4^+.

The greatest disadvantage of this classical method is the incompleteness of the separations.

NEW METHOD

The method whose use we recommend employs, in principle, a reaction which is made specific for each ion, without the need for any prior separation. A large number of cations can thus be detected in the initial solution. The alkaline earths and the alkalis should be detected after separation of the ions of the other groups.

The advantages arising from the practically complete suppression of separations are the following:

(1) The quantity of solution required is very small, nearly all the detections being made on one drop.

(2) The quantities of reagents necessary are likewise very small.

(3) Precipitations are very few and it is rarely necessary to wash the precipitate.

(4) The use of hydrogen sulphide is eliminated.

(5) The different parts of the analysis are quite independent of one another. In cases of doubt, it is a simple matter to repeat any test.

(6) Finally the analysis is vastly more rapid than by the classical method; a complete analysis can be made in the course of 2 hours, and with sufficient practice in the course of 1 hour.

Preparation of the solution for the detection of cations.—The reactions involved in the detection of cations (reactions by the classical method or by the new method) can sometimes be inhibited by the formation of complexes with certain anions such as F^-, CN^-, $C_2O_4^{2-}$, etc. Oxidant or reductant anions can also interfere. Before commencing the qualitative analysis of cations, the solution is freed from interfering ions (see p. 331) and in this way an HCl solution containing no other anions than SO_4^{2-}, ClO_4^-, and H_3PO_4 and HBO_2, which it has not been possible to eliminate, is obtained. The detection reactions are therefore to be considered as taking place in such a solution.

OTHER AUXILIARY METHODS OF DETECTION

A certain number of physical methods is of value in particular cases of qualitative analysis: spectrography, electrography, radioactivity, polarography. These methods are adapted from quantitative analysis, and books on this subject should be consulted about them. (See for instance G. Charlot and D. Bezier, *Methodes modernes d'analyse quantitative*, Masson, Paris, 1954.*)

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* English translation in preparation.

CHAPTER III

ANALYSIS OF A SOLUTION

I. THE SOLUTION IS NEUTRAL OR ALKALINE

IT can contain:

(1) *Anions derived from the non-metals:*

F^-, Cl^-, Br^-, I^-, ClO^-, BrO^-, ClO_3^-, BrO_3^-, IO_3^-, ClO_4^-, IO_4^-;
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, $S_2O_8^{2-}$;
NO_2^-, NO_3^-;
PO_4^{3-};
$C_2O_4^{2-}$, CO_3^{2-}, CN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, CNS^-;
SiO_3^{2-}, SiF_6^{2-};
BO_2^-;

together with organic ions and compounds.

(2) *Anionic derivatives of the metals, certain cations and hydroxides, and complexes.*

Detection of anions in a neutral or alkaline solution

N.B.—A certain number of oxidants and reductant anions can coexist in neutral and alkaline solution, because the rate of reaction of the majority of oxidants is practically zero under these conditions. When the solution is acidified, however, these oxidants and reductants react with one another and the composition of the solution is then considerably affected.

Preliminary tests.—It is useful to examine the solubility of the silver salts (of the anions) in neutral and 4N-HNO_3 solution, and likewise the solubility of the barium salts in neutral solution if possible, and also in 4N-HCl. In this way the presence or absence of certain anions can be established.

(1) *Solubility of silver salts*

    (a) *Silver salts of low solubility in 4N-HNO_3:* those of the anions: Cl^-, Br^-, I^-, yellowish; CN^-, IO_3^-, BrO_3^-, $Fe(CN)_6^{3-}$, orange; $Co(CN)_6^{3-}$; CNS^-; N_3^-; S^{2-} black, oxidized to SO_4^{2-} by boiling with nitric acid; ClO^- gives AgCl in acid solution.

    (b) *Soluble silver salts:* NO_3^-, ClO_3^-, ClO_4^-, $S_2O_8^{2-}$ decomposes slowly, F^-, SiF_6^{2-}.
        NO_2^- and SO_4^{2-} give fairly soluble silver salts.

    (c) All other anions give *silver salts whose solubility in water is low but which are soluble in HNO_3.* Some of these are coloured: the phosphate and arsenite are yellow, the dichromate, chromate, and arsenate are brick red.

    (d) *Silver salts whose solubility in conc. NH_3 is low:* I^-; S^{2-}; CN^-; $Fe(CN)_6^{4-}$ when present in large quantity.

(2) *Solubility of the barium salts*

    (a) *Barium salts whose solubility in dilute HCl is low:* SO_4^{2-}, SiF_6^{2-}, SeO_4^{2-}; IO_3^- and F^- if present in large quantity.

    (b) *Soluble barium salts:* NO_3^-, ClO_3^-, ClO_4^-, $S_2O_8^{2-}$ (gives $BaSO_4$ in the hot); NO_2^-, S^{2-}, $CH_3CO_2^-$, HCO_2^-, CNO^-, Cl^-, ClO^-, ClO_2^-, Br^-, I^-, CN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, CNS^-, N_3^-.

(3) The other anions give barium salts of *low solubility in water, but soluble in HCl.*

Note.—Some anions can form complexes with Ag^+ and, as a result, precipitation may not occur if there is not a sufficient excess of Ag^+.

Certain anions are destroyed in acid solution.

Detection of anions.—The anions derived from the non-metals are then detected individually, if present, by means of the reactions described heretofore.

Part of the solution is taken to dryness on the water bath, then on the sand bath, before looking for borate and chloride.

A portion of the dry residue is ignited in the flame on a spatula: if organic substances are present, carbon and combustible vapours are formed.

Other ions to be detected. Elimination of interfering anions

The solution is acidified with HCl and evaporated to dryness on the water bath. The object of this is to decompose certain substances which are not stable in acid solution: $HClO$, $HBrO$, H_2S, H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $S_2O_8^{2-}$, HNO_2, H_2CO_3, HCN. The residue is taken up in a little conc. HCl and the evaporation to dryness repeated in order to eliminate HF, HI, HBr, HNO_3 and HCNS, and to reduce ClO_3^-, MnO_4^- (reddish violet), $Cr_2O_7^{2-}$ (orange), H_2SeO_4, and H_2TeO_4 and also to insolubilize the silica.

Notes.—In the course of this operation, volatile chlorides may be lost, $HgCl_2$ partially, $AsCl_3$ and $SbCl_3$ and $SeCl_4$ completely. These must be sought in a separate portion of the material, which is not subjected to the acid evaporation treatment.

If $C_2O_4^{2-}$ or organic substances are found, they should be destroyed before going on with the analysis. To do this, the residue should be heated on a sand bath, but in this way some oxides are formed which are rendered insoluble in acids; volatile compounds are lost, $HgCl_2$ for example.

The oxalates and a certain number of organic substances can be destroyed by conc. HNO_3. Evaporate to dryness on the water bath and repeat the operation until nitrous fumes come off. Only after this can the operation be repeated with $HClO_4$ alone, which is taken to boiling point to complete the oxidation and drive off the HNO_3.

If fluorides are present they must be eliminated by heating the residue in a platinum crucible with conc. sulphuric acid until white fumes no longer come off; $BaSO_4$, $SrSO_4$, $PbSO_4$ remain insoluble. The mixture can also be heated with perchloric acid, until white fumes appear, an operation which should be done in a platinum vessel; in order to avoid explosions as a result of the reduction of the $HClO_4$ in the hot, *it is strongly recommended* to make a preliminary attack with conc. HNO_3 and then to

add the $HClO_4$ and to heat on the sand bath. HF is driven off and organic substances are destroyed. ClO_4^- does not interfere in the rest of the analysis.

In all cases the residue is taken up with 2N-HCl, warmed for a few minutes and filtered. A residue A (p. 332) and a solution in HCl B (p. 332) are finally obtained.

II. THE SOLUTION IS ACID

Detection of derivatives of the non-metals.—The following compounds may be present: ClO_4^-, Cl^-, Br^-, I^-, F^-, ClO_3^-, $HBrO_3$, HIO_3, HSO_4^-, HIO_4, NO_3^-, H_3PO_4, $H_2C_2O_4$, CNS^-, $H_2Fe(CN)_6^{2-}$, $Fe(CN)_6^{3-}$, SiF_6^{2-}, HBO_2 and organic compounds.

These can be detected as before. However, certain derivatives of the metals can interfere and are usually separated by making the solution alkaline (phenolphthalein). In this way, a solution similar to that obtained in the preceding case is obtained but the possible number of compounds in it is smaller.

Detection of metallic derivatives.—The solution is treated as on page 331; evaporate to dryness in HCl obtaining the residue A and the solution B. Organic substances, oxalates, and fluorides should be eliminated.

Analysis of residue A.—Characterization of the elements whose chlorides are of low solubility. The washed precipitate contains the chlorides of silver, lead, thallium, and mercurous mercury. It can contain WO_3; basic salts of antimony and of bismuth which are soluble in 4N-HCl; silica.

On diluting with boiling water $PbCl_2$, and with more difficulty $TlCl$, pass into solution. In a portion, white $Pb(OH)_2$ or $PbSO_4$ are precipitated, the former with ammonia, the latter with an alkali sulphate: from another portion, yellow TlI is precipitated (see p. 246).

The residue is taken up with an excess of ammonia. The presence of Hg_2Cl_2 is indicated by a blackening of the precipitate. The ammoniacal solution contains $Ag(NH_3)_2^+$ and WO_4^{2-}. It is acidified sufficiently to re-precipitate AgCl and then reduced with stannous chloride to detect tungsten after possible separation and addition of much HCl.

The insoluble residue is taken up by conc. HCl in order to redissolve the basic salts of bismuth and antimony. Silica remains. A drop of solution placed on a piece of tin foil indicates the presence of Bi(III) or Sb(III) by a black stain. If the test is positive the presence of Sb(III) is confirmed with rhodamine B (p. 228) and Bi(III) by means of stannite (p. 217).

Analysis of the HCl solution B.—It can contain, apart from the majority of cations, SO_4^{2-}, ClO_4^-, HBO_2, H_3PO_4 (we shall suppose for simplicity that stable ionic complexes such as $Ag(CN)_2^-$, $Co(CN)_6^{3-}$, are absent).

DETECTION OF CATIONS IN A SOLUTION

Cations are detected by the methods described in the course of this book. About 0·1 g of the substance in 10 ml of the solution should be available. The solution is neutralized to commencement of precipitation (HCl ≤ 2·5N). It is important to observe these two conditions.

Detection of powerful reductants.—The reaction with methylene blue is carried out (see p. 232). If this is reduced, before carrying out the test the whole of the solution should be oxidized with a little bromine water of which the excess should be driven off by heating. Fe, Sn, As, Sb, V, Re, Mo, W, U are converted to a higher state of oxidation. NH_4^+ can be oxidized.

Preliminary tests.—These rapid tests make it possible to establish in certain cases the absence of groups of ions as a result of which the analysis can be considerably simplified.

(1) Precipitation by ammonia, then by sodium sulphide

Reagents

Ammonia, 6N(1/1).   Saturated sodium sulphide.

Procedure.—(*a*) Add a drop of ammonia to a drop of solution in a microcone. A certain number of hydroxides, and sometimes of phosphates and arsenates, can precipitate. These precipitations are of low sensitivity (0·01M to 0·001M). Absence of a precipitate indicates the absence of more than the indicated quantities of the following ions (units: g.-ions/litre).

Be(II) white (10^{-2}); Hg(II) white (2.10^{-3}); Al(III) white (3.10^{-2}); Ti(IV) white (10^{-2}); Zr(IV) white (5.10^{-3}); Th(IV) white (5.10^{-3}); Ce(III) white (5.10^{-3}) turns yellow in the air; rare earths (III); Sb(III) white (5.10^{-3}); Bi(III) white (5.10^{-3}); Cr(III) green to violet (4.10^{-2}); U(VI) yellow (10^{-2}); Fe(III) rust (5.10^{-3}); Mn(II) brown precipitate, formed slowly (2.10^{-2}); Sn(IV) white (10^{-1}); Tl(III) rust. Cu(II) and Ni(II) give a blue solution, (5.10^{-3}) for Cu(II) and (10^{-1}) for Ni(II); centrifuge.

(*b*) Add a drop of sulphide. Certain sulphides are formed.

Those that are black give sensitive colorations.

Black sulphides: Hg(II) dissolves in the reagent; Bi(III) 5.10^{-4}; Fe(III) and Fe(II) 10^{-3}; Cu(II) 10^{-3}; Ni(II) and Co(II) 5.10^{-4}; Pb(II) 5.10^{-4}; Tl(III) 10^{-4}.

U(VI) brown; Zn(II) white; Cd(II) yellow; Ga(III) white; Mn(II) pink; In(III) yellow, 10^{-2}–10^{-3}.

The precious metals, Se(IV), and Te(IV) give coloured precipitates.

Certain hydroxides remain: Ti(IV), Zr(IV), Th(IV), rare earths, Cr(III).

(2) Precipitation by cupferron.—In HCl of about 1·5N a certain number of ions precipitate.

Reagents

6 per cent aqueous cupferron, freshly prepared.   4N-HCl.

Procedure.—In a microcone add a drop of acid to a drop of solution and then a drop of reagent. Wait 30 seconds.

Sensitivity and selectivity.—The following precipitate, if present in quantities larger than those indicated. $Sn(IV)$ 10^{-4}; $Zr(IV)$ 10^{-4}; $Fe(III)$ 2.10^{-4}; $V(V)$ 3.10^{-4}; $Mo(VI)$ 3.10^{-4}; $Ga(III)$ 5.10^{-4}; $Ti(IV)$ 5.10^{-4}; $Bi(III)$ 5.10^{-4}; $W(VI)$ 5.10^{-3}.

In the absence of a precipitate these ions are present at concentrations lower than indicated above.

(3) **Precipitation by α-benzoin oxime** (see p. 240).

(4) **Precipitation by ammonium sulphate** (see p. 150).

Test on the HCl solution B.—Detect the following ions in the order indicated:

NH_4^+	By Nessler reagent—page 140
Fe^{2+} (and Fe^{3+})	By *o*-phenanthroline—page 167
$V(IV)$, $V(V)$, $Ti(IV)$ . . .	By hydrogen peroxide—pages 177, 236
Mn^{2+} and Ce^{3+}	By oxidation with persulphate in acid —page 192
$Hg(II)$	With Cu foil—page 220
$Bi(III)$	With stannite—page 217
$Zn(II)$, $Co(II)$, $Cu(II)$ . . .	With mercurithiocyanate—pages 200, 202,
Fe^{3+}, Co^{2+}	By thiocyanate—page 165
$Mo(VI)$	By stannous chloride and thiocyanate —page 240
$W(VI)$	By stannous chloride—page 240
H_3PO_4	By molybdate reagent—page 302
$As(III)$ and $As(V)$	By molybdate reagent and reduction to AsH_3—page 224
Fe^{2+}	By dimethylglyoxime—page 166
Ni^{2+}	By dimethylglyoxime—page 196
Cr^{3+} and Ce^{3+}	By oxidation in alkali—page 171
$Zr(IV)$	By azoarsinic derivative—page 179
Be^{2+}	By morin—page 160
Rare earths and $Th(IV)$ . .	By oxalic acid—page 173
$Al(III)$	By aluminon—page 156; or, in the presence of Be^{2+}, by chrome blue—page 158
Ga^{3+}	By chrome blue—page 185
$Sb(III)$ and $Sb(V)$	By rhodamine B—page 228
$Sn(IV)$	By iodine, iodide, and starch—page 230
Cd^{2+}	As sulphide—page 205
UO_2^{2+}	As ferrocyanide—page 183
Pb^{2+}	As sulphide—page 215
K^+	By cobaltinitrite after suitable separation—page 139
Na^+	As triple acetate after suitable separation—page 141

The alkaline earths and alkalis are detected after separation (see p. 190).

Reagents required for the detection of cations.—We give here a list of the compounds necessary for the analysis of cations. The method of preparing the solutions has been indicated for each ion in Part II.

Caustic soda (10N)
Ammonia (14N)

Concentrated acids:
Acetic (17N)
Hydrochloric (12N)
Nitric (14N)
Perchloric (10N)
Sulphuric (36N)
Ammonium sulphide (4N)
    „   chloride
    „   sulphate
    „   oxalate
    „   thiocyanate
    „   molybdate
    „   acetate
    „   nitrate
    „   phosphate (di-)
Sodium sulphide
    „   carbonate
    „   fluoride
    „   thiosulphate
    „   bisulphite
    „   persulphate
    „   acetate
    „   pyrophosphate
    „   tartrate
    „   sulphate
    „   cobaltinitrite
Disodium phosphate
Potassium cyanide
    „   iodide
    „   ferrocyanide
    „   chromate
    „   periodate
Barium chloride
Silver nitrate
Mercuric chloride
Arsenic acid or arsenate
Zirconyl chloride

Ferrous sulphate
Stannous chloride
Copper sulphate
Zinc chloride
    „   acetate
Uranyl acetate
Zinc carbonate
Lead acetate
Ferric chloride
Iodine
Iron powder
Copper foil
Aluminium foil
Antimony (powder)
Hydrogen peroxide (100 vols.)
Universal indicator paper

Organic reagents
95 per cent alcohol
Benzyl alcohol
Ethyl acetate
Oxalic acid
Tartaric acid
Methylene blue
Cupferron
o-phenanthroline (or 2.2-dipyridyl)
N-phenylanthranilic acid
α-benzoin oxime
Dimethylglyoxime
Diphenylcarbazide
p-dimethylaminoazophenylarsonic
    acid
Morin
Aluminon
Chrome blue (colour index 202)
Rhodamine B
Sodium rhodizonate (or 'THQ')
Cinchonine
Thiazole yellow
Starch

Note.—These reagents should be as pure as possible.

Reagents for the detection of anions

General reagents: These are the same as for the detection of cations.

Special reagents:

Sulphuric-chromic mixture
    20 g CrO_3 + 90 ml water + 60 ml
    conc. H_2SO_4
Zirconium nitrate
Alizarin S
Starch iodide paper
Carbon tetrachloride
Potassium dichromate, ground
Fluorescein paper

Soluble starch
Potassium nitrite
Lead peroxide
Zinc powder
Diphenylamine 0·5 per cent in conc.
    H_2SO_4
Potassium permanganate solid
    „   „   solution, 0·01M
Titanium (IV)

Lead carbonate paper
Sodium nitroprusside
Hydrogen peroxide (20 vols.)
Saturated zinc sulphate
Cadmium acetate
Magnesium ribbon
Ferrous o-phenanthroline
Acetate buffer
Strontium chloride, M
Sodium bisulphite, M
Ferrous sulphate, solid
Silver sulphate, saturated
Griess reagents:
    (A) α-naphthylamine
    (B) Sulphanilic acid dissolved separately in 30 ml acetic acid + 70 ml water
Sodium azide

Molybdate-tartrate reagent
Baryta water
Copper sulphate
Ferric chloride
Potassium fluoride, solid
Methyl alcohol
Quinalizarin
Silica, pure
Aniline
o-toluidine
Zinc powder
Silver nitrate
Cobalt acetate
Indigo carmine
Lead acetate
    ,,   nitrate
Methylene blue

ANALYSIS OF A SOLID

DETECTION OF ANIONS

Experiments on the solid

(a) **General tests.**—These tests, which are not essential, can give indications which are a help in orienting the following tests.

(1) *Action of warm M-sulphuric acid.*—Liberation of gas, H_2S from sulphides, HCN from cyanides and certain complexes, NO_2 from nitrites, SO_2 from sulphites and thiosulphates, CO_2 from carbonates and cyanates, O_2 from peroxides, etc.

Addition of sulphuric acid can cause redox reactions; certain compounds then disappear and others appear; thus iodine can be obtained from iodide + oxidants, etc.

(2) *Action of hot conc. sulphuric acid.*—The following can happen:

(a) Liberation of a colourless gas: HF, HCl, HBr and HI fuming in the air.

(b) Liberation of SiF_4 giving H_2SiO_3 with water.

(c) Liberation of SO_2 from sulphites and thiosulphates or from the reduction of H_2SO_4 by S, C, etc., HCNS.

(d) Liberation of CO from oxalates, ferrocyanides, cyanates, and certain organic salts.

(e) Liberation of coloured gases: Cl_2 from chloride + oxidant; Br_2; I_2; CrO_2Cl_2 from chloride + chromate; NO_2 from nitrites and nitrates.

(f) Organic substances can carbonize.

N.B.—ClO_3^-, ClO_4^-, MnO_4^- are dangerous when treated with hot conc. H_2SO_4.

(b) **Special tests.**—Look for the following compounds in the powder:

Phosphates	Attack with conc. HNO_3; molybdate-tartrate reagent (p. 302)
Borates	Methyl borate, p. 321
Chlorides	Chromyl chloride (p. 263); oxidation, liberation of chlorine (p. 262)
Bromides	Oxidation, liberation of bromine (p. 263)
Iodides	Oxidation, liberation of iodine (p. 264)
Fluorides and oxalates . . .	Attack on glass; alizarin-zirconium reagent (p. 257)
Sulphides	By HCl, liberation of H_2S (p. 281)
Fluosilicates	Silicon fluoride (p. 318)
Silicates	Add KF; silicon fluoride (p. 318)
Carbonates	Liberation of CO_2 (p. 310)
Sulphites and thiosulphates . .	Liberation of SO_2 (p. 286)
Nitrites	Liberation of NO_2 (p. 298)

Dissolution in water.—Detect the following anions in the aqueous solution: Cl⁻, Br⁻, I⁻, ClO_3^-, ClO_4^-, SO_4^{2-}, NO_2^-, NO_3^- (see p. 337).

The reaction of the solution to litmus can give indications because the salts of weak acids are basic.

$PbCl_2$, $PbBr_2$, PbI_2, $Pb(CNS)_2$ crystallize on cooling; TlCl can precipitate.

Dissolution in HCl.—SO_4^{2-} coming from $PbSO_4$ can be sought.

Permanganates can interfere by virtue of their colour; reduce them.

Treatment with sodium carbonate.—The preceding solution or the solid can be heated with a solution of M sodium carbonate to the boil for 5 minutes. The majority of anions are then in the solution, and nearly all the metals in the precipitate.

The solution can then be used, after neutralization if necessary, for the detection of anions, in particular of oxalate.

A certain number of anions of compounds which are difficult to attack are not brought into solution in the tests indicated above. They are found after alkaline fusion of the dried residue insoluble in acids (see p. 340), SO_4^{2-} of $BaSO_4$, etc.

DETECTION OF CATIONS

Preliminary treatment of a solid.—If the preceding tests have shown oxalates, organic compounds or fluorides to be present, treat as indicated on page 331. Same notes.

Dissolution in water.—Take 0·1 g of very fine powder; boil with 2 ml of water for 5 minutes; centrifuge; decant through a filter and repeat the operation so long as something dissolves.

Note.—Water can decompose a certain number of substances with liberation of gases; this applies to certain carbides, phosphides, hydrides, sulphides, peroxides, nitrides, etc.

Dissolution in HCl.—Repeat the operation on the residue with conc. HCl. (Volatile $AsCl_3$ may be lost.) If an undissolved residue remains take a small portion of the solid and see if attack by HNO_3 or by aqua regia gives a better result.

Dissolution with perchloric acid.—The solid can be treated with perchloric acid, since the perchlorates are soluble. If silicates are present a mixture of $HClO_4$ + HF in a platinum crucible can be used; silica goes off as H_2SiF_6. If there is danger of explosion by external heating, the solid should be subjected to a preliminary attack by conc. HNO_3. Then add $HClO_4$ and HF and heat until white fumes of perchloric acid appear.

Note.—If oxidation by $HClO_4$ has occurred, low-solubility chlorides may precipitate.

Mix the solutions obtained. The treatment of the undissolved residue will be given later on.

Preliminary treatment of the solution.—If the solution contains silicates, the silica must be rendered insoluble. For this add HCl, if not already present, and evaporate to dryness on the water bath.

If the solid has been attacked with nitric acid or aqua regia, get rid of the majority of the nitric acid in the same way. The residue is then

taken up with 2N-HCl, a solution is obtained and possibly an insoluble residue. These operations will eliminate the following interfering ions: MnO_4^-, NO_2^-, NO_3^-, etc. However, during evaporation in the presence of HCl, $HgCl_2$, $SnCl_4$, $SbCl_3$ can be lost and $AsCl_3$, Se(IV), Te(IV), $AsCl_3$ can escape when boiling with conc. HCl. These elements should therefore be sought in a separate portion.

If the solution does not contain either silicate or interfering ions it is sufficient to add HCl, if not already present, and to separate, if it comes down, the precipitate of low-solubility chlorides.

In both cases the analysis is carried on in the same way.

Treatment of the insoluble residue.—(A) **Characterization of the elements whose chlorides are of low solubility** (see p. 332).

(B) **Characterization of the elements having soluble chlorides** (B) (see p. 333).—0·1 g of powder should be present in about 10 ml.

RESIDUE NOT ATTACKED BY ACIDS

It will contain the following, if present in the initial material: all the $BaSO_4$, AgI, AgCN, SiO_2, silicates, TiO_2, ZrO_2, Nb_2O_5, Ta_2O_5, WO_3, SnO_2, Sb_2O_5, Sn phosphate, CaF_2, $PbCrO_4$ (ignited), SiC, C, S, and part of the $SrSO_4$, $CaSO_4$, $PbSO_4$, AgCl, and AgBr.

In addition, if a natural or calcined product is involved all the possible metals may be found in the residue as well as a certain number of anions (sulphates, carbonates, phosphates, borates, fluorides, cyanides, etc.).

The complex cyanides can be brought into the solution by hot dilute caustic soda.

Treatment of the residue.—The residue is brought into the solution by dry fusion.

Use of a platinum crucible.—A large number of compounds attack platinum: As, Sb, P, S, alkalis and oxidants, etc.; Ag, Pb, Sn, Hg, Au, Bi give fusible alloys.

These elements should be absent when the solid is fused in a platinum crucible. A systematic treatment of the residue with aqua regia eliminates all these elements, with the exception of Ag, Sn (and sometimes Pb).

The platinum crucible should be heated on a clean refractory triangle and never over a luminous flame. The molten mass should not occupy more than one-third of the crucible. To clean such a crucible, melt pyrosulphate in it. The sides can be rubbed with a fine powder such as precipitated calcium carbonate or sulphate but never with a hard object (stirring rod, etc.).

Before using the platinum crucible it is necessary to burn the sulphur and carbon. Lead sulphate should be looked for as well as silver compounds. (A drop of alkaline sulphide turns them black.) Lead is completely dissolved by a hot solution of 4N ammonium acetate and silver salts with KCN solution. The treatment should be continued until nothing more goes into solution. Detect $PbSO_4$ in one part, Cl^-, Br^-, I^-, Ag^+ in the other part of the solution.

Detection of tin.—Tin should be looked for in the residue. If it has been shown to be absent in the initial powder, this operation can be omitted. If not, a little of the residue is mixed with 5 or 6 times its volume of KCN.

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The mixture is placed in a small porcelain crucible, covered, and heated on a Meker burner. (N.B.—If oxidizing substances are present there may be an explosion. Be careful of cyanide vapours. Use a fume cupboard.) Allow to cool, take up with water and separate the metallic grains formed. Dissolve the metal with HNO_3; a white precipitate of stannic hydroxide will be left.

Attack by molten alkali carbonates.—The residue, very finely powdered, is mixed with 4–6 times its weight of a mixture of equal parts of sodium and potassium carbonates (eutectic with lowest melting point). Heat the covered crucible to bright redness and stir. When the evolution of CO_2 ceases, allow to cool on a sheet of clean iron, then dissolve the boiling water in a small beaker. Filter, wash with dilute sodium carbonate. Dissolve the insoluble matter with HCl.

Note.—If a platinum crucible is not available a nickel crucible may be used. This is always attacked, with formation of nickel oxide, which will be found in the analysis.

Analysis of residue.—Examine the carbonate solution for: F^-, SO_4^{2-}, S^{2-}, CN^-, BO_2^-, PO_4^{3-}, WO_4^{2-}, AlO_2^-, CrO_4^{2-}, SiO_3^{2-} (see p. 330). Examine the acid solution for the following: alkaline earths, Ti(IV), Zr(IV), Fe(III), etc. (see p. 333).

Other methods of attack.—If the attack with carbonate is not successful, the following methods can be tried:

Fusion with $S + Na_2CO_3$.—This is the better method of attack for SnO_2. Heat a part of the residue in a porcelain crucible with 6 parts of a mixture of equal weights of sulphur and sodium carbonate. Cover. Heat for about 20 minutes with a small flame.

After cooling take up in water and then filter. The aqueous solution contains all the elements giving sulphide anions or complexes which are stable in alkali.

The insoluble contains the oxides and sulphides whose solubility in alkali is low.

Fusion with Na_2O_2.—Nickel crucible (for chromite, corundum, SnO_2, SiC, etc.); use 5 times the weight of sodium peroxide. Heat to fusion for 20 minutes. Dissolve in water; boil to destroy hydrogen peroxide. Filter.

The solution contains all the elements which give anions stable in alkali after oxidation.

This method of attack is very efficacious.

N.B.—**Goggles are essential.**

Fusion with pyrosulphate.—TiO_2, Fe_2O_3, Al_2O_3, Cr_2O_3, etc. Heat the mixture with 10 times its weight of pyrosulphate, preferably in a silica crucible. Heat gently until the melt is completely clear. Take up with $9N$-H_2SO_4.

It is sometimes necessary to use $H_2SO_4 + HF$ in a platinum crucible either to drive off silica (and boron) or to dissolve with formation of complexes. Then evaporate to dryness and fuse with pyrosulphate in the platinum crucible.

Flame colorations

In conc. HCl a drop of the solution held in a loop of platinum wire and inserted into the flame gives the following colorations:

Na . . .	Yellow. Very sensitive reaction.	Hg_2Cl_2 . . Violet.
		Pb . . . Pale blue.
Ca . . .	Reddish orange. Also very sensitive.	Cu . . . Blue to green.
		As—Sb . . Bluish white.
		Se . . . Pale blue.
Sr . . .	Bright red.	Tl . . . Green.
Li . . .	Bright red.	Te . . . Green.
K . . .	Pale violet.	Ba . . . Pale green.
Rb . . .	Violet.	H_3BO_3 . . Green.
Cs . . .	Blue-violet.	H_3PO_4 . . Green.
Ga . . .	Violet.	Mn . . . Green.
CN^- . . .	Mauve.	Ba . . . Pale green.

Attack of alloys

Steels and cast-iron.—These always contain: C, carbides and graphite; silicides and silicon; P, S, Mn. They can contain many metals, Ni, Cr, W, Mo, V, Co, etc., and can be very difficult to attack.

(1) Attack with conc. HCl. PH_3, AsH_3, SiH_4, H_2S are liberated;

(2) Attack with HNO_3.

(3) Attack with aqua regia.

(4) Special steels are attacked by $HClO_4$ at its boiling point (attack first with HNO_3).

Bronzes and brasses.—0·1 g of filings or turnings is attacked with 5 ml of 6N nitric acid. Concentrate to small volume and take up with 10 ml of water. The insoluble contains SnO_2, Sb_2O_5 (and a little Cu, Pb, Fe, P, Bi). Treat it with sodium sulphide on the water bath and centrifuge. The insoluble from this treatment will contain Bi_2S_3, PbS, CuS, FeS and the solution Sn, Sb, P.

White metals.—Pb, Sn, Sb. They can be attacked by hot conc. sulphuric acid ($PbSO_4$ dissolves). The solution is diluted and treated with NaOH and Na_2S. Use can also be made of HCl + Br_2.

Light alloys.—Si, Al, Al-Cu, Mg, etc. They can be brought into solution either with HCl or NaOH.

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DECIMAL LOGARITHMS

	0	1	2	3	4	5	6	7	8	9
1	00	04	08	11	15	18	20	23	26	28
2	30	32	34	36	38	40	42	43	45	46
3	48	49	51	52	53	54	56	57	58	59
4	60	61	62	63	64	65	66	67	68	69
5	70	71	72	72	73	74	75	76	76	77
6	78	79	79	80	81	81	82	83	83	84
7	85	85	86	86	87	88	88	89	89	90
8	90	91	91	92	92	92	93	94	94	95
9	95	96	96	97	97	98	98	99	99	100

This table gives the logarithms, to base 10, for the numbers from 1 to 100, and will be found useful for expressing concentrations, etc., in logarithmic form.

ATOMIC WEIGHTS

Actinium . . .	Ac	227	Molybdenum .	Mo	96·0
Aluminium . .	Al	26·98	Neodymium . .	Nd	144·3
Americium . .	Am	243	Neon	Ne	20·18
Antimony . .	Sb	121·8	Neptunium . .	Np	237
Argon . . .	A	39·94	Nickel . . .	Ni	58·7
Arsenic . . .	As	74·9	Niobium . .	Nb	92·9
Astatine . . .	At	210	Nitrogen . . .	N	14·01
Barium . . .	Ba	137·4	Osmium . . .	Os	190·2
Berkelium . .	Bk	245	Oxygen . . .	O	16·00
Beryllium . .	Be	9·01	Palladium . .	Pd	106·7
Bismuth . . .	Bi	209·0	Phosphorus . .	P	30·98
Boron . . .	B	10·82	Platinum . . .	Pt	195·2
Bromine . . .	Br	79·9	Plutonium . .	Pu	239
Cadmium . .	Cd	112·4	Polonium . .	Po	210
Calcium . . .	Ca	40·1	Potassium . .	K	39·10
Californium . .	Cf	246	Praseodymium .	Pr	140·9
Carbon . . .	C	12·01	Promethium . .	Pm	147
Cerium . . .	Ce	140·1	Protactinium .	Pa	231
Cesium . . .	Cs	132·9	Radium . . .	Ra	226·0
Chlorine . . .	Cl	35·46	Radon . . .	Rn	222
Chromium . .	Cr	52·0	Rhenium . . .	Re	186·3
Cobalt . . .	Co	58·9	Rhodium . . .	Rh	102·9
Copper . . .	Cu	63·5	Rubidium . .	Rb	85·5
Curium . . .	Cm	243	Ruthenium . .	Ru	101·7
Dysprosium . .	Dy	162·5	Samarium . .	Sm	150·4
Erbium . . .	Er	167·2	Scandium . .	Sc	44·96
Europium . .	Eu	152·0	Selenium . . .	Se	79·0
Fluorine . . .	F	19·00	Silicon . . .	Si	28·09
Francium . .	Fa	223	Silver	Ag	107·9
Gadolinium . .	Gd	156·9	Sodium . . .	Na	23·00
Gallium . . .	Ga	69·7	Strontium . .	Sr	87·6
Germanium . .	Ge	72·6	Sulphur . . .	S	32·07
Gold	Au	197·0	Tantalum . .	Ta	180·9
Hafnium . . .	Hf	178·6	Technetium . .	Tc	99
Helium . . .	He	4·00	Tellurium . .	Te	127·6
Holmium . . .	Ho	164·9	Terbium . . .	Tb	158·9
Hydrogen . .	H	1·008	Thallium . . .	Tl	204·4
Indium . . .	In	114·8	Thorium . . .	Th	232·1
Iodine . . .	I	126·9	Thulium . . .	Tm	169·0
Iridium . . .	Ir	192·2	Tin	Sn	118·7
Iron	Fe	55·85	Titanium . . .	Ti	47·90
Krypton . . .	Kr	83·8	Tungsten . . .	W	183·9
Lanthanium . .	La	138·9	Uranium . . .	U	238·1
Lead	Pb	207·2	Vanadium . .	V	50·95
Lithium . . .	Li	6·94	Xenon . . .	Xe	131·3
Lutecium . .	Lu	175·0	Ytterbium . .	Yb	173·0
Magnesium . .	Mg	24·32	Yttrium . . .	Y	88·9
Manganese . .	Mn	54·9	Zinc	Zn	65·4
Mercury . . .	Hg	200·6	Zirconium . .	Zr	91·2

PERIODIC CLASSIFICATION OF THE ELEMENTS

I a	I b	II a	II b	III a	III b	IV a	IV b	V a	V b	VI a	VI b	VII a	VII b	VIII	VIII b
1. H															2. He
3. Li		4. Be		5. B		6. C			7. N		8. O		9. F		10. Ne
11. Na		12. Mg		13. Al		14. Si			15. P		16. S		17. Cl		18. A
19. K		20. Ca		21. Sc		22. Ti		23. V		24. Cr		25. Mn		26. Fe / 27. Co / 28. Ni	
	29. Cu		30. Zn		31. Ga		32. Ge		33. As		34. Se		35. Br		36. Kr
37. Rb		38. Sr		39. Y		40. Zr		41. Nb		42. Mo		43. Te		44. Ru / 45. Rh / 46. Pd	
	47. Ag		48. Cd		49. In		50. Sn		51. Sb		52. Te		53. I		54. Xe
55. Cs		56. Ba		57–71. Rare Earths		72. Hf		73. Ta		74. W		75. Re		76. Os / 77. Ir / 78. Pt	
	79. Au		80. Hg		81. Tl		82. Pb		83. Bi		84. Po		85. At		86. Rn
87. Fr		88. Ra		89. Ac		90. Th		91. Pa		92, 93, 94, etc., Transuranium Elements					

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